PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

OCTOBER 1888.

I. *Note on the Conditions of Self-Excitation in a Dynamo Machine.* *By* SILVANUS P. THOMPSON, *D.Sc.**

WHEN about the year 1867 it began to be recognized that a machine constructed on the principle of magneto-electric induction might be made to excite the magnetism in its own field-magnets, it became usual to explain the phenomenon of self-excitation in language something like the following. There being a small amount of residual magnetism in the core of the stationary electromagnet, very feeble currents will be induced in the secondary or armature-coils when they are set into rotation at any given speed. If these feeble induced currents are now sent round the coil of the fixed electromagnet they will exalt its feeble magnetism, and its inductive action will be stronger ; these stronger currents being also sent round the magnet will raise its magnetism still higher, and so by action and reaction the magnetism and the currents grow at a compound-interest rate until the limit fixed by the magnetic saturation of the iron core of the field-magnet is reached.

Long before the true rationale of the limit of self-excitation was assignable, it was known that this method of considering the subject was faulty. Were it true, it would follow that,

* Read May 12, 1888.

no matter what the speed of driving, or the resistance in the electric circuit, the magnetism would go on rising until the iron had attained saturation. The facts, on the contrary, are (1) that in self-exciting machines the degree of excitation of the field-magnets depends most emphatically on the speed and on the resistances of the electric circuit; (2) that for machines which have their exciting coil in series with the armature and main circuit, there is a certain relation between speed and resistance such that they do not excite themselves at all unless the quotient of speed by resistance attains a certain minimum value; (3) that in machines which have their exciting coil connected as a shunt to the main circuit there is again a certain relation between the speed and the electric resistances of the various parts of the circuit, such that with a given speed self-excitation does not take place unless the resistance of the external circuit exceeds a certain limiting value.

On June 26, 1886, I had the honour of bringing before the Physical Society* some formulæ relating to the performance of dynamo-electric machines, in which this matter was touched upon, and in which, on the assumption that the law of magnetization might be adequately represented by the Lamont-Frölich formula, expressions were obtained for the relations between speed, magnetization, resistance, and current. As an important conclusion it was shown, always upon the above assumption, that at a given speed of driving and with a given resistance in the electric circuit, the current, of any given series-wound machine, was always less by a certain fixed quantity than that current which would have been produced (at that speed and with the given resistance) had the magnetism been actually at full saturation. This difference between the actual current and the current that there would have been at saturation was a definite number of amperes, and was shown to be that number of amperes which would have been sufficient to produce exactly half-saturation in the given machine. This half-saturating number of amperes I had previously denominated the "Diacritical" current. This proposition having been established, it became obvious that the machine would not excite itself if the speed and resistance were such—the speed so low or the resistance so high—that

* See Proc. Phys. Soc. vol. viii. p. 76.

the current which would have been produced with field-magnets independently saturated was less than the diacritical current. Or, if the resistance of the circuit were prescribed, there would obviously be a least-speed of self-excitation.

The assumption in the above investigation of an approximate expression for the law of magnetization necessarily made the argument less satisfactory than would be the case were no such assumption made. In the argument which follows no assumptions are made of an empirical character as to the law of magnetization, absence of secondary phenomena, such as electric and magnetic leakage, being the only point assumed.

It is known that the electromotive force of a dynamo may be written

$$E = nCN; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the electromotive force (in absolute C.G.S. units); n the number of revolutions of the armature per second; C the number of conductors counted round the periphery of the armature, and closed in series; N the whole number of magnetic lines (in C.G.S. units) that traverse the armature.

So, writing ΣR for the sum of the electric resistances (in C.G.S. units) of the circuit in which the electromotive force operates, the current flowing in the circuit may be written as

$$i = \frac{nCN}{\Sigma R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Again, it is known that the number of magnetic lines in the armature may be calculated by dividing the line-integral of the magnetizing forces by the sum of the magnetic resistances of the "magnetic circuit" of the dynamo. If the machine is joined up with its exciting coil of S convolutions in series with the main circuit, the line-integral of the magnetizing forces will be written as $4\pi Si$. Then, writing $\Sigma\rho$ as the sum of all the magnetic resistances in the magnetic circuit, we shall have

$$N = \frac{4\pi Si}{\Sigma\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (2) we get

$$\frac{i}{N} = \frac{nC}{\Sigma R}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and, from (3),

$$\frac{i}{N} = \frac{\Sigma\rho}{4\pi S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Equating (4) and (5), we have

$$4\pi S n C = \Sigma\rho \, . \, \Sigma R. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It will be noticed that this equation contains neither N nor i, and its truth is independent of the relation between i and N. It is true that $\Sigma\rho$, which is a factor of the expression on the right-hand side, depends on N, and, in general, increases when N is increased. But the truth of the equation is not affected by the form of the relation between $\Sigma\rho$ and N; in brief, it is true independently of any assumptions as to the form of the law of magnetization.

On examining the expression on the left hand of the equation, it will be seen that, for a given dynamo, all its factors, except the speed n, are invariable. Hence the main fact brought out by this equation is that in a series dynamo, driven at constant speed, the product of the magnetic resistance into the electric resistance is a constant. We have here the key to the behaviour of the self-exciting dynamo;—the explanation why it is that the machine, though exciting itself up "at a compound-interest rate," stops short of absolute saturation in the degree to which its magnetization is raised. As the field-magnets get more and more highly magnetized, the magnetic resistance increases. Suppose that such a dynamo, running at a constant speed, works at a certain degree of magnetization when there is a certain resistance in the electric circuit. Suppose that resistance to be now reduced: the current increases; as a result there is higher magnetization, higher electromotive force, and therefore still greater current. To what point will these things go on increasing? Equation (6) gives the answer: until the decrease in the electric resistance is exactly balanced by the increase in the magnetic resistance.

Other phenomena of the action of the dynamo now become more intelligible. As is well known, in ascending magnetizations of iron there is a certain stage at which the magnetic permeability increases, instead of decreasing, with an increase in the magnetization. In a dynamo at this stage of excitation,

any increase in the electric resistance, causing a decrease in the current, will also cause an increase in the magnetic resistance ; hence this stage of excitation is one of instability. The dynamo is either excited above this stage, or else its excitation falls below this stage—virtually to zero.

The two factors of the product $\Sigma\rho \,.\, \Sigma R$ are both complex quantities, containing constant as well as variable terms. We may write

$$\Sigma\rho = \alpha + \xi.$$

Here the constant part α relates to the magnetic resistance of the gap between the armature-core and the polar surface of the field-magnets ; which gap, filled partly with copper, partly with air, and partly with insulating materials, possesses, so far as is known, a constant magnetic resistance. The variable part ξ of the magnetic resistance relates to the iron portions of the magnetic circuit : it is in general the sum of a number of terms such as $l/\mu A$, where l is the length, A the sectional area, and μ the permeability, for the time being, of the various portions—cores, yoke, &c.

Similarly, we may write

$$\Sigma R = a + x ;$$

where a stands for the constant part of the electric resistances (armature and main-circuit coils) in the circuit, and x for the variable part ; that is to say, the resistance of the external circuit, including under that term not only true ohmic resistances, but also the effects of counter electromotive forces opposed in the path of the current of the machine.

We may now rewrite equation (6) in the following form for the series-wound machine driven at a constant speed :—

$$(\alpha + \xi)(a + x) = \text{constant}. \quad . \quad . \quad . \quad . \quad (7)$$

Now at starting, when as yet the magnetization of the iron is almost zero, the resistance of the iron part of the magnetic circuit is small. Its value is not indeed quite zero, but depends upon the prior history of the iron. It is certainly so small as to be negligible compared with the value of α. Hence there will be a particular maximum value of x, which we may call x_1, corresponding to the case when $\xi = 0$. This maximum value, which will be given by the equation

$$x_1 = \frac{4\pi n \mathrm{CS}}{\alpha} - a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

will be the critical external resistance of the machine at the prescribed speed. If any greater resistance than x_1 be intercalated in the circuit the machine will refuse to excite itself, even though there is a small initial magnetization present. So far as there is a weak magnetization present, the machine will act as a feeble magneto-electric machine.

Suppose, now, that x is so far decreased that the total electric resistance is reduced to half its limiting value, that is to say, let $x' = \frac{1}{2}x_1 - \frac{1}{2}a$: then the current and the magnetization will both run up until the magnetic resistance is equal to double its initial value, and ξ will have the value $\xi' = \alpha$. The permeability of the magnetic circuit, taken as a whole (iron, copper, and air), will have been halved. This state of things corresponds to the "diacritical point" in the excitation first investigated by the author in 1884 ; and, if the Lamont-Frölich formula were true, this point would correspond to the state of semi-saturation of the magnetization.

Again, suppose the variable part of the electric resistance to be reduced to zero ; in other words, let the machine be short-circuited. Then ξ will run up to the maximum value it can have at that speed. Calling this value ξ_2, we have

$$\xi_2 = \frac{4\pi n \mathrm{CS}}{a} - \alpha. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It is further clear that if a fixed value be given to the external electric resistance x, there will be a limit in speed below which the machine will refuse to excite itself, the least-speed of self-excitation (called by some authorities the "dead turns," by others the "critical velocity") being given by the equation

$$n_1 = \frac{\alpha(a+x)}{4\pi \mathrm{CS}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This throws some light on the observed fact that very small machines are not self-exciting except at very high speeds. The fixed part α of the magnetic resistance varies in similar machines of different size, inversely as the linear dimensions ; also the fixed part a of the electric resistance varies inversely as the linear dimensions of the machine. Hence the least-speed of self-excitation in similar machines (on short-circuit) varies inversely as the square of the linear dimensions. In

practice it is possible, in larger sizes of machine, to reduce both α and a to amounts relatively smaller; for the actual air-space left for clearance may be relatively smaller in large machines, and a relatively greater thickness of copper on the armature-periphery is admissible. When the machine is on short-circuit, $x=0$, and the last equation then becomes

$$n_1=\frac{\alpha a}{4\pi \mathrm{CS}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This, too, is important as showing that the least-speed of self-excitation of a machine while short-circuited is a measure of the goodness of the magnetic circuit.

For a shunt-wound dynamo the fundamental equation becomes

$$(\alpha+\xi)\left(a+s+\frac{as}{x}\right)=4\pi n\mathrm{CZ}; \quad . \quad . \quad . \quad (12)$$

where a is, as before, the resistance of the armature-circuit within the machine, s the resistance of the exciting shunt-circuit, and Z the number of convolutions of the shunt-coil. Excitation does not take place at a given speed n unless x has as its *minimum* value

$$x=\frac{\alpha as}{4\pi n\mathrm{CZ}-\alpha(a+s)}. \quad . \quad . \quad . \quad . \quad (13)$$

On open circuit, when $x=\infty$, the least-speed of self-excitation is

$$n_1=\frac{\alpha(a+s)}{4\pi \mathrm{CZ}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the machine then exciting itself through its own circuit as a series-machine. If short-circuited it will require an infinite speed to become self-exciting.

There is a still more general way of establishing the relation (6). Every dynamo may be regarded as an arrangement of two circuits, a primary (or field-magnet) circuit and a secondary (or induced or armature) circuit, between which there is a coefficient of mutual induction M, which is caused to vary by mechanically altering the configuration of the system. If the currents in the two circuits be called respectively i_1 and i_2, then the work done in starting or stopping either current in the presence of the other is equal to $\mathrm{M}i_1i_2$. Now in each revolution of the armature of an ordinary dynamo

the current in each of the sections of the armature-coil is twice started and twice stopped. Hence in each semi-revolution the work to be mechanically performed in driving is equal to Mi_1i_2; or if, as in the series-dynamo, the current in the two circuits is the same, the work to be done is Mi^2. Now, on the assumption that there is no magnetic leakage, the value of M is equal to $4\pi S_1S_2 \div \Sigma\rho$; where S_1 and S_2 are the respective numbers of convolutions of the primary and secondary coils which surround the tubes of magnetic force in the magnetic circuit. For our purpose, S_2, in ordinary armatures, with symmetrically-wound coils united in a self-closed circuit, tapped at two opposite points by the two contact-brushes, and with commutation occurring at points where each commuted convolution encloses a maximum magnetic flux, is equal to $\frac{1}{2}C$. But the work done by the machine in the electric circuit during a semi-revolution is equal to $i^2\Sigma R \div 2n$. Equating this to the work done on the machine gives, as before,

$$\Sigma\rho \,.\, \Sigma R = 4\pi n CS.$$

City and Guilds Technical College,
Finsbury, June 1888.

II. *On a Simple Apparatus for the Measurement of the Coefficients of Expansion by Heat.* *By* Prof. W. E. Ayrton, *F.R.S.*, *and* Prof. J. Perry, *F.R.S.**

The apparatus consists of a metal tube within which the wire or rod, whose coefficient is to be determined, is placed. One end of the wire is rigidly attached to one end of the tube, and the other end connected to an Ayrton and Perry magnifying-spring, a pointer attached to which indicates the change of length due to alteration of temperature. Steam or water may be passed through the tube, the temperature of the wire being shown on a thermometer. The arrangement is very sensitive, and with a pointer about 20 centim. long the motion is magnified about 1000 times.

A magnifying-spring attached to an aneroid was also shown and its great sensibility demonstrated. A combination of a

* Read May 12, 1888.

spring of large diameter and pitch with one of small diameter and pitch was exhibited. By such a combination small rotations can be immensely magnified. The great features of the patent spring as a magnifier are the entire absence of friction and back lash, and the large range of proportionality.

III. *On a New Barometer, called "the Amphisbæna."* *By* T. H. Blakesley.*

This instrument consists of a straight glass tube of uniform internal cross section, closed at one end and open to the atmosphere at the other. A thread of quicksilver occupies a portion of the tube, the space between the quicksilver and the closed end being occupied by air. A uniformly graduated scale, of any convenient dimensions, *but whose zero point is coincident with the closed end*, is attached. Since there is no escape for the air contained between the quicksilver and the closed end, this scale serves to determine the volume of this air at any particular moment. The instrument can be suspended vertically with the closed end either upwards or downwards, and in these positions the volumes of the cushioned air, as indicated by the end of the quicksilver thread, can be ascertained. It is clear that when the closed end is upwards this air is subject to a pressure which is the difference between the atmospheric pressure and that due to a column of quicksilver equal in height to the length of the thread. But when the closed end points downwards, the pressure of the cushioned air is the sum of the atmospheric pressure and that due to the length of the thread.

These two observations, then, enable one to find the relation between the atmospheric pressure and that due to the thread of quicksilver.

Let H be the unknown height of the barometer;
l be the length of the thread of quicksilver;
A be the reading of the volume of air enclosed, when the closed end of the tube is upwards;
B be the reading of the volume, when the closed end is downwards.

* Read June 23, 1888.

Then the product of the pressure and volume being the same in the two cases, assuming the temperature constant,

$$(H-l)A=(H+l)B,$$

or

$$H=\frac{A+B}{A-B}l.$$

Thus the following rule applies :—Divide the sum of the readings by their difference, and multiply by the length of the quicksilver thread.

Since the length of the quicksilver occurs as a factor, it is obviously advantageous that it should be a simple number, as 10 inches. Where centimetres are required, 25 centimetres or 50 centimetres would be convenient quantities.

Here it may be pointed out that the usual correction for temperature may be made once for all, by having the thread of quicksilver, not exactly 10 inches or 50 centimetres, but such a length as would be 10 inches or 50 centimetres at zero of temperature Centigrade. Then, by taking the simple number for use in the calculation, whatever the real length may, on account of temperature, be, the final result is the *reduced* barometer.

A convenient length for a portable instrument would be about 20 inches, with a 10-inch thread of quicksilver.

The diameter of the tube should be small enough to maintain continuity in the quicksilver. 1·2 millim. or one twentieth of an inch answers very well.

The value of an observation made with this instrument would theoretically not be injured should the quicksilver thread become, through mischance, discontinuous, so long as all the liquid remained in the tube, though it appears that practically the multiplication of ends by subdivision adds a certain amount of friction, and produces sluggishness in the movements of the quicksilver.

In using the instrument for determining mountain elevations, the length of the quicksilver may be left quite undetermined ; for the difference of level appears as a function of the *ratio* merely of the two pressures at the points of observation $\left(\mathfrak{H}\log\frac{p_1}{p_2}\right)$, where $\mathfrak{H}$ is the height of the homogeneous

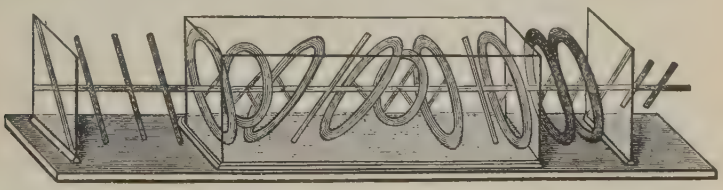
atmosphere. Therefore we can use the ratio of the functions $\left(\frac{A+B}{A-B}\right)$ of the *observations only* at the two stations.

In practice the glass tube is sunk into a groove in a light piece of wood provided with two eyes, which serve either for suspension from a nail in a wall, or for attaching a strap or cord for slinging the instrument round the shoulders in climbing. The eye at the open end of the tube will screw in far enough to stop the opening temporarily if that should be desirable; but if care is taken to climb with the closed end downwards, there is small fear of the quicksilver becoming either lost or discontinuous.

The instrument, as made by Messrs. Watson Brothers, of 4 Pall Mall, weighs between 6 and 7 oz.

IV. *On an Optical Model.* *By* Prof. A. W. Rücker, *F.R.S.**

The model exhibited and described is to illustrate the character of the vibrations in a crystal cut parallel to the axis, when plane-polarized light is incident upon it. A rectangular glass box represents the crystal, and glass plates placed at



short distances from each end imitate crossed Nicols. A rod carrying coloured circular and elliptical rings and straight bars passes along the axis of the box. These rings are intended to indicate the character of the vibration at the different points at which they are placed. The length of the crystal is supposed to be such that plane-polarized red rays emerge plane-polarized in the initial plane after being successively plane, elliptical, circular, elliptical plane, elliptical circular, elliptical and plane-polarized within the crystal. All the light is quenched by the analyzing Nicol. Supposing another kind of light (say

* Read June 23, 1888.

green) to be used, another rod with green ellipses &c. is placed in the box, and illustrates that such light may emerge elliptically polarized, one component only being stopped by the analyzer. This shows how plane-polarized white light, when passed through crystals placed between Nicols, may become coloured.

V. *A Design for a Standard of Electrical Resistance.* *By* J. A. Fleming, *M.A., D.Sc., Professor of Electrical Technology in University College, London**.

[Plate I.]

In designing a standard of electrical resistance the two points to which attention is directed are the choice of the material in which the standard is embodied, and the form or disposition of the instrument.

Experience is yet far from complete as to the entire permanence of wires of alloys over prolonged periods of time when employed as standards of electrical resistance ; but having regard to the inconveniences which attend the use of mercury in standards intended to be conveyed about, evidence, as far as we have it, points to the tolerable permanence of the platinum-silver alloy (66 p.c. of silver + 32 p.c. of platinum) when drawn into wire, for use as the material substance of which the actual standard is made.

A definite length and gauge of standard wire has then to be so arranged that, whilst kept at a constant temperature, currents can be passed through it and the resistance between certain points ascertained.

The form which has hitherto been chiefly manufactured, and which is in most general use, is the form of standard which was designed by the Committee of the British Association on the original introduction of the B.A. unit, and shown in plate 4 of the 'Reprint of Reports on Electrical Standards,' by Prof. Fleeming Jenkin. In this form of standard the actual coil is wound on a bobbin consisting of a tube of thin brass having ebonite cheeks. Attached to these cheeks are the two long bent copper rods which serve as the electrodes,

* Read November 10, 1888.

held in position by a distance-piece of ebonite. In order that the coil may be immersed in a medium of known temperature it is further enclosed in a thin shell of brass consisting of a double tube (see fig. 1), and the whole shell filled up with paraffin wax or ozokerit. Some makers then place a thin lid of ebonite on the top of the shell.

Experience gained by a rather extensive use of standards of resistance of this form has indicated to the writer that this design can be, with some advantage, modified. The disadvantages of the present B.A. form of standard are as follows:— When in use the standards must be placed in water of a known temperature or in melting snow or ice. After a sufficiently prolonged time the temperature of this water can be taken, and the temperature of the water will be the temperature of the wire of the standard, assuming that equilibrium of temperature has been attained. If a current is now passed through the coil in order to take a measurement of its electrical resistance, the temperature of the wire is raised, and its resistance is altered.

Other things being equal, the best design of coil is that in which this electrically developed heat is got rid of by diffusion as quickly as possible. The embedding of a coil in a large mass of badly-conducting material like paraffin or ozokerit is, from this point of view, a great disadvantage.

Sufficient electrical insulation has to be provided ; but this should be achieved without the use of more enveloping insulation than necessary.

The two chief objections to the B.A. form of standard are, however, these :—

First, it cannot be placed in water with the shell wholly under water or under ice without short-circuiting the electrodes, and, when used as intended, whilst the narrow or bottom portion of the coil is in the water, the upper and more massive portion is in the air, and therefore may be at a different temperature to the bottom portion. Hence arises a doubt as to the actual temperature of the coil of wire. It has to be borne in mind that the limitation of accuracy in such comparisons of standards of resistance is determined by the difficulty of ascertaining temperature, and not in the mere measurement of resistance. Uncertainty as to the actual temperature of the

wire to the extent of one or two tenths of a degree Centigrade renders nugatory elaborate arrangements for very accurate measurement of resistance.

Second. The standards, as at present constructed, are liable to another defect. If the standard is being used in melting ice or snow, and therefore cooled to 0° Cent., deposition of dew will take place upon the upper surface, whether the ebonite lid or paraffin-wax surface, through which the copper-rod electrodes protrude. The copper rods are originally lacquered or varnished, but when the lacquer wears off, any film of moisture so deposited will short-circuit the electrodes and reduce the observed resistance. In comparing standards in melting ice, either then the whole shell must be as far as possible placed under the melting ice, in which case stirring the liquid may splash water on to the surface of the paraffin, or else the shell has to be only partly immersed, in which case ambiguity exists as to the actual temperature of the coil of wire.

These and some other difficulties, such as that of keeping a rather deep vessel of melting ice at a constant temperature, have impressed on the writer the necessity for modifying the form of the standard, and one form which has proved itself to be very satisfactory in use is as follows :—The case or shell which contains the coil is in the form of a ring (see fig. 5). This ring consists of a pair of square-sectioned circular troughs provided with flanges which can be screwed together so as to form a square-sectioned, hollow, circular ring.

From this ring proceed upwards two brass tubes about five or six inches in length. Down these brass tubes pass the copper electrodes or rods, and these rods are insulated from the tubes at the top and bottom by ebonite insulators. The insulator at the bottom of the tube, where it enters the ring, is a simple collar, that at the top has the form of a funnel corrugated on its outer surface. The use of this funnel will be referred to presently. The actual resistance-coil is a length of platinum-silver wire three-fold silk-covered. The silk-covered wire is first baked above 100° C. to dry it completely, and then immersed in melted ozokerit or paraffin.

The so insulated wire is cut about the proper length and laid double or folded once upon itself and then rolled up on a wooden mandril so as to form a circular coil of diameter

suitable to drop into the hollow of the brass ring. The wire being wound double, its coefficient of self-induction is rendered very small. This coil of wire is then wrapped over with white silk and again dipped in melted ozokerit. The ends of the wire are next soldered into nicks in the ends of the copper rods, they having been previously pushed a little way through the brass tubes for the purpose, and afterwards drawn back into proper positions. The coil is then packed into the circular groove, and, after adjusting the resistance to the proper value, the bottom half of the ring is placed over it. A thin washer of indiarubber is inserted between the flanges, and the whole screwed tightly together. The resistance-coil is thus enclosed in a thin ring of metal, and can be placed wholly below the surface of water or ice. In order to test the tightness of the joints, a little test-pipe is provided on the upper surface of the ring. By placing the ring coil below water and blowing into the test-pipe, the good fitting of the joints can be assured. The aperture of this test-pipe is afterwards closed by solder or a screw (see fig. 6).

Apart from the insulation of the coil itself it will be apparent that the insulation is limited by the amount of insulation resistance secured at the ebonite insulators at the top end of the brass tubes. Any leakage from the copper rod over these insulators to the brass tube destroys to that extent the insulation of the coil. The object of making these external insulators funnel-shaped is to prevent surface creeping, due to condensation of moisture on them, by placing paraffin oil or insulating liquid in the funnel-shaped cavity. When this is done, even if dew should collect on the outer surface of the funnels, the inner surface is kept dry by the paraffin oil placed in them, the action being the same as that in the well-known Johnson and Phillip's fluid insulator.

The ring-coils when in use are placed in rather shallow zinc troughs, which can be filled with water, and which are closed with a wooden lid. When so placed the whole of the actual coil or resistance part is down beneath the liquid at one level, where the temperature can be accurately ascertained. The insulators and point of emergence of the electrodes are away up above the level of the water, and well protected from any action which might permit of leakage over them

The large metallic mass of the ring assists in bringing the resistance-coil quickly back to the temperature of the surrounding water, and the coil therefore "tests quickly." In all other respects these standards of resistance are as compact and portable, and not more expensive to construct than the old form of B. A. standard, whilst obviating the difficulties which present themselves in the use of the old form in very accurate comparisons of resistance.

Other forms of standard coil which have been tried are indicated in figs. 2, 3, and 4, but have not proved themselves to be as convenient as that above described and illustrated in figs. 5 and 6.

It is quite possible to have two or more coils of wire inside the same ring, each coil having its separate pair of electrodes. A useful coil of this form can be made up containing 1, 10, and 100 ohms, so that comparisons can be quickly made at the same temperature with these three multiples of the same unit of resistance.

The adjustment of the coils to a certain value presents no great difficulties. The wire is in the first instance cut a little longer than required, and its resistance nearly adjusted; when the two ends of the coil have been soldered to the lower ends of the copper rods, the resistance is again taken from the ends of the electrodes. This resistance should be a little greater than the final value required. The middle point of the wire or extreme loop is now stripped of its silk and the loop twisted up with the pliers, the resistance being carefully taken at intervals. When just a very little in excess of the value required the twisted coil is touched with solder, and having been bound over with insulating material the coil is completed. In the construction of standards it is obvious that it is not so important that the resistance should have an exact integer value at any temperature as that its value at some temperature and its coefficient of variation of temperature should be exactly known.

VI. *On the Upper Limit of Refraction in Selenium and Bromine.* *By* Rev. T. Pelham Dale, *M.A.**

In my former paper read before the Society† I showed that the value of the limit could be found by the solution of the equation

$$a \sin\theta = \sin m\theta ;$$

where a is the ratio of wave-lengths in free æther, and $\theta = \frac{\pi h}{l}$, h being what I there called the molecular distance, and l the corresponding wave-length within the medium. If $a \sin\theta$ be greater than unity, the solution is imaginary.

It was also shown that if ν be limit of refraction, μ the index corresponding to θ, that

$$\frac{\mu \sin\theta}{\theta} = \nu.$$

If $\theta = \frac{\pi}{2}$, we have

$$\mu = \frac{\pi}{2}\nu ;$$

μ being the index of the limit of refraction towards the violet end of the spectrum. Call this the upper limit, and denote it by μ_k.

$\therefore$ $\mu_k - \nu$ is the total dispersion

$$= \left(\frac{\pi}{2} - 1\right)\nu ;$$

also

$$\frac{\mu_k - 1}{d} = \text{constant independent of temperature.}$$

Also by the relation

$$\frac{\pi h}{l} = \theta,$$

we have for l_k the upper limit

$$\frac{\pi h}{l_k} = \frac{\pi}{2},$$

or

$$2h = l_k.$$

Hence the quantity h is half the wave-length within the medium of the limiting transmissible ray.

* Read November 10, 1888.

† Proc. Phys. Soc. vol. ix. p. 167.

As also

$$\sin\theta = \frac{\lambda}{\lambda_1}\sin\theta_1,$$

or

$$\frac{\lambda}{\lambda_1} = a,$$

we have at the limit

$$\frac{\lambda}{\lambda_k}\sin\theta = \sin m\theta,$$

$$= \sin\frac{\pi}{2} = 1;$$

$$\therefore\ \lambda\sin\theta = \lambda_k.$$

If on further examination this upper limit should be established as a physical entity it will modify our ideas of dispersion, which we must then regard as identical with refraction.

There is a relation between the Eulerian integral $\Gamma(n)$ and $\frac{\sin\theta}{\theta}$ which is worthy of notice,

$$n\pi = \theta.$$

By a well-known relation,

$$\Gamma n\,.\,\Gamma 1-n = \frac{\pi}{\sin n\pi}.$$

Hence

$$\Gamma(1+n)\Gamma(1-n) = \frac{n\pi}{\sin n\pi}.$$

If a table of $\Gamma(1+n)$ is at hand, it can be used as a practically expeditious method of finding the value denoted by θ*.

Also if for n we write $1-n$ in the above, we have

$$\Gamma(1+1-n)\big(\Gamma 1-(1-n)\big) = \frac{\pi-n\pi}{\sin(\pi-n\pi)},$$

or

$$\frac{1-n}{n}\Gamma(1+n)\ \Gamma(1-n) = \frac{\pi-\theta}{\sin(\pi-\theta)},$$

which gives us

$$\frac{\sin(\pi-\theta)}{\pi-\theta} = \frac{n}{1-n}\cdot\frac{\sin\theta}{\theta}.$$

Now since $\sin(\pi-\theta)$ is equally a solution of the equation, $a\sin\theta = \sin m\theta$, it is probable therefore that this solution may have a physical meaning.

* The tables of logarithms by Vassal containing a column of circular measures of arc serve every purpose as far as calculation is concerned.

It was noticed in my former paper that, of the substances for which data were at hand, selenium alone had its upper limit within the visible spectrum. Accordingly a fresh calculation of the values of θ_k, ν, and λ_k were made and the results given below (Table I.).

It will be seen from the table that the limiting wave-length which is transmissible is $\lambda = 5295{\cdot}7$. This is a little below λ_E, which is 5269·13. It was of great interest to observe how far this purely theoretical result would be supported by observation. As neither temperature nor specific gravity of specimen were given, and the indices of refraction to the third place of decimals only, it was evident that, as a preliminary experiment, all that could be sought for was a general agreement.

With this in view I had a Browning amateur spectroscope-eyepiece fitted to my microscope, an old instrument constructed many years ago by Troughton and Sims. After a few trials I succeeded in obtaining a tolerably uniform film of selenium mounted as an ordinary microscope-slide. The film when cold was quite transparent, and transmitted a deep ruby tint. This film was found under the spectroscope to transmit rays nearly to the line D. Another and thinner slide was prepared. Under the microscope the thinner portions were found to be of a more orange tint, due to a spectrum reaching to the beginning of the green. Even in brilliant sunlight no sensible extension beyond this took place. In parts of the film were holes. If these were in the field they appeared as spectra extending to the violet end, but with sharp well-defined sides, showing apparently that a very thin film was effective to stop all the upper rays. Thus, then, the agreement of theory and observation seems as satisfactory as could be anticipated, considering both the data and instrumental means employed.

The examination of sulphur gave similar results. Here the limiting wave-length lies beyond the visible spectrum. A film of melted sulphur transmits yellow light. This film darkens rapidly as the temperature rises, and when the sulphur begins to boil, it, as is well known, assumes a brownish tint. Examined under the spectro-microscope, it is seen that the absorption is confined to the violet end. If the film be

placed boiling under the spectro-microscope, the spectrum is seen to be generally darkened till near the red end, and the violet quite cut off. As the film cools, the resulting dark cloud seems to recede towards the violet. If the film be very thin it appears colourless to the eye, and under the spectroscope the violet is visible. It remains colourless after the sulphur has crystallized, appearing nearly white to the eye. Selenium also darkens rapidly by heat and then transmits a greyish light, which is probably due to its breaking up into crystals. It has, however, the property of becoming more transparent as it cools. Thus the optical properties of these two substances are as remarkably similar as are their chemical relations.

It will be observed that the quantity $\frac{\nu-1}{d}$, though by no means the same in both selenium and sulphur, are not far apart. There is, however, another relation which exists ; it is expressed by the formula, that in selenium,

$$\nu_{Se}-1=(\nu_S-1)\frac{E}{d};$$

where ν_S is limit of refraction of sulphur, E its equivalent, and d its density. That is, that the refraction-equivalent of selenium can be found by multiplying the refraction-equivalent of sulphur by the equivalent of selenium divided by the density of that element. This is worthy of remark, as it appears that the same relation within five or six units in the second place of decimals between isobutyl iodide as compared with isobutyl chloride, and orthobromotoluine compared with chlorotoluine and benzyl chloride. With regard to benzyl chloride, I may mention that calculation for the upper limit has revealed an error due to extracting the wrong logarithm of sin θ_A. The correct result given below agrees better with the rule that $\frac{\nu-1}{d}$ is constant in isomeric bodies. As in the case of two isomeric bodies, the equivalent is the same in both, it will be seen that this result is in agreement with the relation between selenium and sulphur stated above.

It is worthy of note that chlorine and bromine resemble sulphur and selenium in tint of transmitted light. The index

of refraction for the line A in bromine is $\mu_A = 1{\cdot}6260$. It occurred to me that it would be possible to obtain a probable idea of the spectrum of this element by assuming an upper limit of refraction. Taking this limit as D and F, to which I subsequently added G, I found that F gave $\theta_A = 39° 44'$, $\nu = 1{\cdot}4988$, and the refraction-equivalent 13·1. Dr. Gladstone, calculating from A, gives as a probable value 15·3, which would necessarily be greater than that obtained from the limit. A refraction-equivalent for ν obtained from orthobromotoluine showed that for this substance the refraction-equivalent for ν was between 14 and 15. If we assume G as the limit, then bromine comes out as 13·7. I subsequently procured a specimen of bromine. In as thin a film as I could produce, the spectra of bromine and selenium were almost indistinguishable; but the tint of bromine is decidedly more orange, and its vapour transmitted rays up to F certainly, and perhaps beyond; but in the brightest sunlight, and even when mixed with air, there was no indication of violet rays. So far as these very imperfect observations extend, they seem to support the conclusions previously arrived at by calculation. Without venturing, then, to speak at all decisively, the subject seems a promising one and likely to repay further investigation.

In the absence of data as to the spectrum of liquid chlorine, it is useless to make calculations as to any relations which might be found to subsist between it and bromine. It is, however, of importance to observe that its yellow tint is so similar to that of sulphur, that it is not improbable that the same portions of the spectrum would be affected in both. If this on further examination should turn out to be the fact, it would be one step more towards the attainment of the form of the function $\mu = \phi(\lambda)$, which would probably reveal relations of great interest toward determining the chemical constitution of bodies.

In the case of the critical angle the imaginary sine corresponds with the change from refraction to total reflexion. And this, again, to alteration of phase in the wave of the polarized ray. Is there anything similar in the limit of refraction? I think there is. If a mirror be constructed by melting selenium on a glass slide and then pressing on it a somewhat cooler glass, we shall obtain a reflecting surface on remo-

ving the glass, and also another on the corresponding surface attached to the glass. At angles near perpendicular incidence the reflected light has a certain greenish tint. This is more apparent on the side next the glass than on the free reflecting surface, but is very evident in both. It is no doubt to be expected that light not transmitted should in certain cases be reflected. If it be absorbed there must be an expenditure of energy within the medium, which we have every reason to believe acts on the wave-length within the medium and the velocity of its transmission. The importance of selenium is that it is a manageable substance, in which the critical point of transmission lies near the middle of the luminous spectrum. Bromine would no doubt prove equally interesting, but is by no means a pleasant substance to handle.

I should hardly have ventured to come before the Society with these very rough experiments, had I not hoped that some who possessed the instrumental means would be induced to make the observations. For my own part I am more than content with the humble though somewhat laborious office of computor between mathematical investigator and observer.

TABLE I.—Comparison of Sulphur and Selenium.

Selenium.						
Density. d.	Lower index. μ_A.	Upper index. μ_D.	Arc. θ_A.	Lower limit. ν	$\frac{\nu-1}{d}$.	Shortest wave-length. λ_k.
4·3	2·653	2·980	44° 9′ 0″	2·3976	32502	5295·7
Sulphur.						
*d.	μ_A.	μ_E.	θ_A.	ν.	$\frac{\nu-1}{d}$	
d' 2·07 d'' 1·98	1·9024	1·9527	20° 32′ 0″	1·8610	41648 43535	

* d' is the density of native sulphur.
d'' „ „ of that from fusion.

Thus we have the following empirical relation. If E be

the equivalent of sulphur, and ν its limit of refraction,

$$\frac{\nu-1}{d'}\mathrm{E}=13326,$$

$$\frac{\nu-1}{d''}=13932.$$

Again, we have

Orthobromotoluine, $\nu-1=5299$,

Ref. equiv. Benzyl chloride $\frac{\nu-1}{d}\mathrm{E}=5941{\cdot}7$,

do. do. Chlorotoluine, $\frac{\nu-1}{d}\mathrm{E}=5907{\cdot}2$,

and

Isobutyl iodide, $\nu-1=4749$,

Ref. equiv. Isobutyl chloride, $\frac{\nu-1}{d}\mathrm{E}=4163{\cdot}9$.

TABLE II.—Bromine.

Spec. grav.	μ_A.	Assumed upper limit.		
		μ_D.	μ_F.	μ_G.
3·085	1·6260	give 10·9	13·1	13·7
		corresponding refraction-equivalents.		

Note on these Tables.—They can only be accepted as approximate, but the calculations have been carried quite as far as the uncertainty of the original data warrant. Under these circumstances the coincidences noticed between sulphur and selenium are of no great value, except perhaps as pointing out a likely direction in which the search for these empirical relations amongst the refractive indices should be pursued.

VII. *On the Calculation of the Coefficient of Mutual Induction of a Circle and a Coaxal Helix.* *By* Prof. J. V. Jones, *M.A., Principal of the University College, Cardiff**.

If M is the coefficient of mutual induction of any two curves, we have

$$M=\iint \frac{\cos\epsilon}{r}\,ds\,ds';$$

where $r=$ the distance between two elements ds and ds', and $\epsilon=$ the angle between them.

Let us take for the equations of the circle and helix :—

$$\left.\begin{aligned} y&=a\cos\theta,\\ z&=a\sin\theta,\end{aligned}\right\} \quad \ldots\ldots\ldots \quad \text{(i.)}$$

$$\left.\begin{aligned} y'&=\mathrm{A}\cos\theta',\\ z'&=\mathrm{A}\sin\theta',\\ x'&=k\theta'.\end{aligned}\right\} \quad \ldots\ldots\ldots \quad \text{(ii.)}$$

Then

$$M=\iint \frac{dx\,dx'+dy\,dy'+dz\,dz'}{\sqrt{(x-x')^2+(y-y')^2+(z-z')^2}},$$

$$=\int_0^{2\varpi}\int_0^{\Theta}\frac{\mathrm{A}a\cos(\theta-\theta')d\theta\,d\theta'}{\sqrt{\mathrm{A}^2+a^2-2\mathrm{A}a\cos(\theta-\theta')+k^2\theta'^2}}.$$

If we change the variables in this integral, putting

$$\theta-\theta'=\phi,$$

$$\theta'=\phi',$$

we find

$$M=\int_{-\Theta}^{2\varpi-\Theta}\int_{-\phi}^{\Theta}\mathrm{V}\,d\phi\,d\phi'+\int_{2\varpi-\Theta}^{0}\int_{-\phi}^{2\varpi-\phi}\mathrm{V}d\phi\,d\phi'$$
$$+\int_0^{2\varpi}\int_0^{2\varpi-\phi}\mathrm{V}d\phi\,d\phi', \qquad \text{(I.)}$$

where

$$\mathrm{V}=\frac{\mathrm{A}a\cos\phi}{\sqrt{\mathrm{A}^2+a^2-2\mathrm{A}a\cos\phi+k^2\phi'^2}}$$

$$=\frac{\mathrm{A}a\cos\phi}{\sqrt{\alpha^2+k^2\phi'^2}},$$

* Read November 10, 1888.

if $$\alpha^2 = A^2 + a^2 - 2Aa\cos\phi,$$

$$= \frac{Aa\cos\phi}{\alpha}\left\{1 - \frac{1}{2}\frac{k^2\phi'^2}{\alpha^2} + \frac{1.3}{2.4}\frac{k^4\phi'^4}{\alpha^4} - \&c.\right.$$

Now

$$\int V\,d\phi' = \frac{Aa\cos\phi}{\alpha}\left[\phi' - \frac{1}{2}\cdot\frac{1}{3}\frac{k^2}{\alpha^2}\phi'^3 + \frac{1}{2}\cdot\frac{3}{4}\cdot\frac{1}{5}\frac{k^4}{\alpha^4}\phi'^5 - \&c.\right]$$

$$= \frac{Aa\cos\phi}{\alpha}[S_{\phi'}],$$

where $S_{\phi'}$ = the series in brackets.

[It may be noticed that

$$S_{\phi'} = \frac{1}{k}\log\left(k\phi + \sqrt{\alpha^2 + k^2\phi^2}\right) - \frac{1}{k}\log\alpha.]$$

It may be shown that $S_{\phi'}$ is convergent if $k\phi' < \alpha$. Now the maximum value of ϕ' is Θ, and the minimum value of α is $A - a$. Hence the series is convergent for all values of ϕ' and α that occur in the second integration if $k\Theta < A - a$. So long as this is the case we shall arrive, after performing the second integration, at a convergent series.

Substituting the above value of $\int V\,d\phi'$ in equation (I.), we have

$$M = \int_{-\theta}^{2\varpi-\theta}\frac{Aa\cos\phi}{\alpha}(S_\theta - S_{-\phi})\,d\phi$$

$$+ \int_{2\varpi-\theta}^{0}\frac{Aa\cos\phi}{\alpha}(S_{2\varpi-\phi} - S_{-\phi})\,d\phi$$

$$+ \int_{0}^{2\varpi}\frac{Aa\cos\phi}{\alpha}(2_{2\varpi-\phi} - S_0)\,d\phi.$$

The sum of the last two of these integrals and the second half of the first is zero ; and hence

$$M = \int_{-\theta}^{2\varpi-\theta}\frac{Aa\cos\phi}{\alpha}S_\theta\,d\phi$$

$$[\text{or } M = \int_{-\theta}^{2\varpi-\theta}\frac{Aa\cos\phi}{\alpha}\log\frac{k\Theta + \sqrt{\alpha^2 + k^2\Theta^2}}{\alpha}d\phi].$$

If Θ is an integral multiple of ϖ (*i. e.* if $\Theta = n\varpi$), we may express M in a series of powers of $\left(\frac{kn\varpi}{A+a}\right)^2$, the coefficients of which are functions of the quantity $\frac{2\sqrt{Aa}}{A+a}$, and the complete elliptic integrals to that modulus.

For in this case

$$M=\int_{-n\varpi}^{2\varpi-n\varpi}\frac{Aa\cos\phi}{\alpha}S\theta\,d\phi$$

$$=2\int_{0}^{\varpi}\frac{Aa\cos\phi}{\alpha}S\theta\,d\phi.$$

The general term in this expression for M is

$$2(-1)^m\frac{1.3.5\ldots\overline{2m-1}}{2.4.6\ldots2m}\,\frac{k^{2m}(n\varpi)^{2m+1}}{2m+1}Aa\int_0^{\varpi}\frac{\cos\phi\,d\phi}{\alpha^{2m+1}}.$$

Now

$$\int_0^{\varpi}\frac{\cos\phi\,d\phi}{\alpha^{2m+1}}=\int_0^{\varpi}\frac{\cos\phi\,d\phi}{(A^2+a^2-2Aa\cos\phi)^{\frac{2m+1}{2}}}$$

$$=-\frac{2}{(A+a)^{2m+1}}\int_0^{\frac{\varpi}{2}}\frac{\cos2\theta\,d\theta}{(1-c^2\sin^2\theta)^{\frac{2m+1}{2}}},$$

where $c=\frac{2\sqrt{Aa}}{A+a}$

$$=-\frac{2}{(A+a)^{2m+1}}P_m,$$

where $P_m=\int_0^{\frac{\varpi}{2}}\frac{\cos2\theta\,d\theta}{(1-c^2\sin^2\theta)^{\frac{2m+1}{2}}}$.

Hence we may write

$$M=-\Sigma4(-1)^m\frac{1.3.5\ldots\overline{2m-1}}{2.4.6\ \ldots\ 2m}\,\frac{k^{2m}}{2m+1}\,\frac{(n\varpi)^{2m+1}}{(A+a)^{2m+1}}AaP_m$$

$$=-4n\varpi\frac{Aa}{A+a}\Sigma(-1)^m\frac{1.3.5\ldots\overline{2m-1}}{2.4.6\ \ldots\ 2m}\,\frac{1}{2m+1}\left(\frac{x}{A+a}\right)^{2m}P_m,$$

where $x=kn\varpi$.

Or, writing down the first few terms of the series,

$$M=-4n\varpi\frac{Aa}{A+a}\left\{P_0-\frac{1}{2}\cdot\frac{1}{3}\left(\frac{x}{A+a}\right)^2P_1\right.$$

$$+\frac{1.3}{2.4}\cdot\frac{1}{5}\left(\frac{x}{A+a}\right)^4P_2$$

$$-\frac{1.3.5}{2.4.6}\cdot\frac{1}{7}\left(\frac{x}{A+a}\right)^6P_3$$

$$+\frac{1.3.5.7}{2.4.6.8}\cdot\frac{1}{9}\left(\frac{x}{A+a}\right)^8P_4$$

$$\left.-\ \&c.\right\}.$$

It now remains to indicate how P_0, P_1, P_2, &c. may be calculated.

Let

$$Q_m = \int_0^{\frac{\varpi}{2}} \frac{d\theta}{(1-c^2\sin^2\theta)^{\frac{2m+1}{2}}}.$$

Then

$$P_m = \left(1-\frac{2}{c^2}\right)Q_m + \frac{2}{c^2}Q_{m-1}, \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

and

$$Q_m = Q_{m-1} + \frac{c}{2m-1}\frac{d}{dc}Q_{m-1}. \quad . \quad . \quad . \quad \text{(III.)}$$

With the help of these two formulæ, observing that

$$Q_0 = F(c),$$
$$Q_{-1} = E(c),$$

and using the relations

$$\frac{dF(c)}{de} = \frac{E(c)}{c(1-c^2)} - \frac{F(c)}{c}$$

and

$$\frac{dE(c)}{de} = \frac{E(c)-F(c)}{c},$$

we may express P_0, P_1, P_2, &c. successively in terms of $F(c)$, $E(c)$, &c. The first three are :—

$$P_0 = \left(1-\frac{2}{c^2}\right)F + \frac{2}{c^2}E,$$

$$P_1 = \left(1-\frac{2}{c^2}\right)\frac{E}{1-c^2} + \frac{2}{c^2}F,$$

$$P_2 = \frac{2-c^2}{3c^2(1-c^2)}F - \frac{2(1-c^2+c^4)}{3c^2(1-c^2)^2}E.$$

I have not expressed P_3, P_4, &c. in terms of F, E, &c., because in practice it is easier to calculate them numerically in any special case as follows, rather than from their expressions in terms of F, E, &c.

(i.) Calculate

$$Q_1, \quad \frac{dQ_1}{dc}, \quad \frac{d^2Q_1}{dc^2}, \quad \frac{d^3Q_1}{dc^3}, \text{ &c.,}$$

or

$$Q_1, \quad \dot{Q}_1, \quad \ddot{Q}_1, \quad \dddot{Q}_1, \text{ &c.}$$

These may be successively calculated from the equation

$$(1-c^2)Q_1 = E$$

and its derivatives :—

$$c(1-c^2)\dot{Q}_1-2c^2Q_1=E-F,$$
$$c(1-c^2)\ddot{Q}_1+\dot{Q}_1(1-5c^2)-3cQ_1=0,$$
$$c(1-c^2)\dddot{Q}_1+4(1-2c^2)\ddot{Q}_1-13c\dot{Q}_1-3Q_1=0,$$
&c.

(ii.) Calculate Q_2, Q_3, Q_4, &c. from the equations :—

$$Q_2=Q_1+\frac{c}{3}\dot{Q}_1,$$

$$Q_3=Q_2+\frac{c}{5}\dot{Q}_2=Q_2+\frac{c}{5}\left\{\frac{4\dot{Q}_1}{3}+\frac{c}{3}\ddot{Q}_1\right\},$$

$$Q_4=Q_3+\frac{c}{7}\dot{Q}_3=Q_3+\frac{c}{7}\left\{\frac{24}{15}\dot{Q}_1+\frac{11}{15}c\ddot{Q}_1+\frac{1}{15}c^2\dddot{Q}_1\right\},$$
&c.,

which are obtained by successive applications of formula (III.).

(iii.) Calculate P_2, P_3, P_4, &c. from these values of Q_2, Q_3, Q_4, &c. by successive applications of formula (II.).

I have performed the calculations for a circle of 5 inches radius situated in the mean plane of a coaxal helix of 10 inches radius and axial length 4 inches.

In this case,

$$A=10,$$
$$a=5,$$
$$x=2,$$
$$c=\quad\cdot942809$$
$$Q_{-1}=E=1\cdot113741$$
$$Q_0=F=2\cdot528625$$
$$Q_1=\quad10\cdot02366$$

$$\dot{Q}_1=\quad156\cdot6023$$
$$\ddot{Q}_1=\quad5419\cdot795$$
$$\dddot{Q}_1=156574\cdot9$$

$$Q_2=\quad59\cdot23901$$
$$Q_3=\quad419\cdot7842$$
$$Q_4=2207\cdot927$$

$$P_0 = \quad \cdot 54870$$
$$P_1 = \quad 6 \cdot 84018$$
$$P_2 = \quad 51 \cdot 4955$$
$$P_3 = 391 \cdot 442$$
$$P_4 = 1613 \cdot 68$$

Hence

$$\begin{aligned} M = n\{&54 \cdot 86225 \\ &- 1 \cdot 69790 \\ &+ \cdot 10226 \\ &- \cdot 00823 \\ &+ \cdot 00041\} \\ = n &\times 53 \cdot 25879 \end{aligned}$$

The above investigation was undertaken in connexion with a measurement of a resistance in absolute measure by the method of Lorenz, which I propose making in the Physical Laboratory at Cardiff. The standard coil which I have constructed for this purpose consists of a helix of copper wire, of diameter ·02 inch, wound in a screw-thread of pitch ·025 inch, cut in our Whitworth lathe on a brass cylinder of diameter 22 inches, the number of turns of wire being 185. For such a coil it seemed probable that Lord Rayleigh's formula, which is a first approximation, might not give a result of sufficient accuracy for the purpose in view; and when Lord Rayleigh, with whom I had the privilege of speaking on the matter last summer, expressed this opinion, it became clear that a formula embodying a closer approximation would have to be worked out. This might be done by considering the helix as a current-sheet, and proceeding to a second approximation on this hypothesis. But it seemed to me preferable to make a direct attempt at integration for the case of helix and circle, though I hardly anticipated that I should arrive in the result at a formula of such simplicity as that given above.

It is interesting to observe that, by Lord Rayleigh's formula, the coefficient of mutual induction of the circle and helix taken above for purposes of calculation comes out to be

$$n \times 53 \cdot 317.$$

The difference between the two results is about one tenth per cent.

Prof. Perry asked if the thickness of the wire had been considered, and whether the author could give any information as to practical working formulæ for the mutual induction between two ordinary cylindrical coils in any position.

Dr. Fleming described a wooden anchor-ring wound like a gramme armature, and having a secondary coil added, which he had devised as a standard of mutual induction, and used for determining capacity absolutely.

In reply the Author said he had not considered the wire to have thickness, as he felt sure this would not affect the result for his coil by one part in 100,000. With respect to Dr. Fleming's anchor-ring, he considered the difficulty of winding it sufficiently uniformly to be a great drawback to its general adoption.

VIII. *On the Measurement of the Luminosity and Intensity of Light reflected from Coloured Surfaces.* *By* Capt. W. de W. Abney, *C.B., R.E., F.R.S.**

In a communication† to the Royal Society General Festing and myself have shown how to compare the light of the different parts of the spectrum reflected from a white surface with that reflected from a coloured surface, and we gave the results of measurements of various colours, and from these constructed their luminosity curves by means of the luminosity curve of the spectrum of white light, which we had ascertained from our previous researches on Colour Photometry (Bakerian Lecture 1886). From the areas of these curves we deduced the total luminosity of these colours, compared with that of a white surface. Certain colours were combined by means of rotating sectors to form a grey, and this was matched with the grey formed by rotating sectors of black and white. By noting the angular value of each coloured sector, and of the black and white sectors, it was found that the luminosity curves of the colours were correct.

This is an indirect, though very accurate, method of ascertaining the luminosity of a coloured surface, and re-

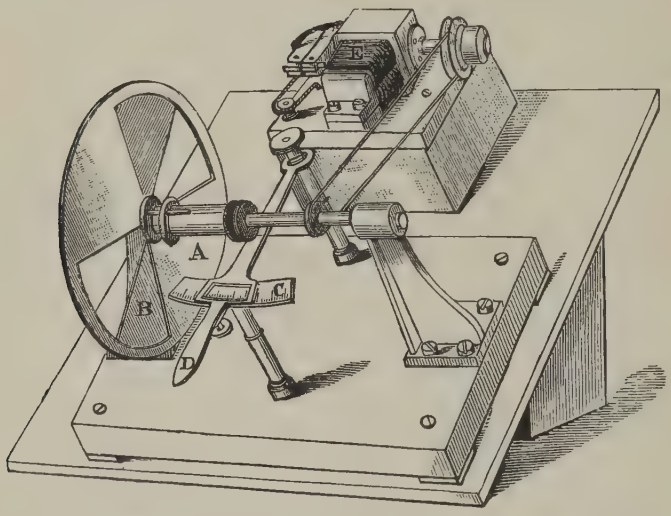
* Read November 24, 1888.

† "Colour Photometry," Part II., Phil. Trans. Part A, 1888.

quires more time than can often be spared with that object in view. Professor O. Rood, in his "Modern Chromatics," indicates the manner in which he proceeds, which is as follows. He finds "that with the aid of rotating disks the second constant of colour (luminosity) can often be determined. Let us suppose we wish to determine the luminosity of paper painted with vermilion: a circular disk about six inches in diameter is cut from the paper and placed on a rotation apparatus . . On the same axis is fastened a double disk of black and of white paper, so arranged that the proportions of black and white can be varied at will. When the whole is set in rapid rotation the colour of the vermilion paper will of course not be altered, but the black and white will blend into a grey. This grey can be altered in its brightness till it seems about as luminous as the red." He then proceeds to give examples. This method must not only be difficult to manage, but also must be tedious before the match can be determined. A method based on the same plan is given later in this paper, which makes the matching of the luminosities more easy.

The following plan, however, I venture to think is much simpler and more certain in result, and is essentially founded on the method which General Festing and myself adopted in measuring the luminosity of the spectrum itself. In that we found that any coloured light might be compared with any other or with white light by *rapidly* changing the luminosity of one colour, when the two were in juxtaposition, making it first decidedly too light and then too dark, and then gradually diminishing the oscillations until an equality of luminosity was obtained. The two colours were placed alongside one another, it may be recollected, by means of the Rumford method of shadows. In the case of the spectrum the rapid diminution in luminosity from the yellow to each end of the spectrum enabled the change of luminosity to be quickly made by sliding the card containing the slit (which allowed a slice of coloured light to pass and to subsequently form a patch of that colour on the screen) along the spectrum on each side of the maximum, and then noting the position of the colour, which balanced a white light of known intensity. In the case of the measurement of the luminosity of coloured paper, this method evidently was inapplicable, and it remained to devise some other.

In our former experiments of the measurement of light reflected from coloured surfaces, General Festing and myself employed rotating sectors, movable when in motion, but the motion was slow, being effected by means of a screw. Mr. Hilger, in whose hands was placed a rough design for an improved set of rotating sectors, produced an instrument in which the sectors would be opened and closed rapidly by means of a simple lever arrangement without any screw-motion. The instrument is shown in the accompanying figure. A, B are the sectors which can be opened at pleasure by means of the lever, D, moving along an arc, C, on which is a scale of degrees. The sectors are rotated by a small electromotor, with sufficient speed to prevent scintillation.



The apparatus at once got over the difficulty of getting a rapid alternation of intensity in any light falling on a surface when the instrument was placed between it and such surface. Supposing the luminosity of a vermilion-coloured surface had to be compared with a white surface when both were illuminated, say, by gas-light, the following procedure was adopted:—A space of such a size was cut out of black paper that one side was rather less than twice the breadth of the rod used to cast a shadow. One half of the aperture was filled with a white surface and the other half with the vermilion-coloured

surface. The light L was caused to illuminate the whole of this, and the rod R placed in such a position that it cast a

shadow on the white surface, the edge of the shadow being placed accurately at the junction of the vermilion and white surfaces. A flat unsilvered mirror M was placed at such a distance and at such an angle that the light it reflected cast a second shadow on the vermilion surface. Between R and L were placed the rotating sectors A B. The white strip was then caused to be evidently too dark and then too light by altering

the aperture of the sectors, and an oscillation of diminishing extent was rapidly made till the two shadows appeared equally luminous. A white screen was substituted for the vermilion, and again a comparison made. The mean of the two sets of readings of angular apertures gave the relative value of the two luminosities. It must be stated, however, that if the screen remained open, as represented, the values would not be correct, since any diffused light which might be in the room would relatively illuminate the white surface more than the coloured one. To obviate this the receiving screen was placed in a box in the front of which a narrow aperture was cut just wide enough to allow the two beams to reach the screen. An aperture was also cut at the front angle of the box through which the observer could see the screen. When this apparatus was adopted its efficiency was seen from the fact that when the apertures of the rotating sectors were

closed the shadow on the white surface appeared quite black, which it would not have done had there been any diffused light in any quantity present within the box. The box, it may be stated, was blackened inside and was used in a darkened chamber. The mirror arrangement was useful, as any variation in the direct light also showed itself in the reflected light. Instead of gas-light, reflected sky-light, the electric light, or sunlight can be employed by very obvious artifices; for it must be remembered that the comparison-light may be of any kind, and distinct, if necessary, from the light illuminating the coloured surface.

General Festing and myself had measured with great care the luminosities of emerald green, vermilion, and ultramarine, which we had combined in a rotation apparatus to produce a grey. The total luminosity of these three colours I measured by the apparatus described, using as the source of light to illuminate the colour, the patch of white light formed by a recombination of the spectrum, the comparison light being an ordinary gas-light.

The following table gives the values obtained by the spectrum method and also by the method I now introduce. It will be seen that the coincidence between the two values is very close:—

Colour.	Area of Luminosity Curves (from Paper in the Phil. Trans.).	Luminosity Readings by New Method.		Value from areas when white =100.	Value from New Plan when white =100.
		Readings.	Mean.		
White	534	73 77, 75, 76	75	100	100
Emerald Green .	221	32, 28, 29, 31, 31	30·2	41·1	40·3
Vermilion	216	33, 30, 29, 29	30·2	40·0	40·3
French Ultramarine.....	49	6, 7, 7, 7·5	6·9	9·2	9·2

For another purpose I had measured the luminosity curves of six different colours by the spectrum method, and below is a table of the intensities of the light of different wave-lengths reflected from each and from a white surface. The areas indicate the total luminosities of the several colours.

Intensity Curves.

Scale No.	Yellow.	Orange.	Red.	Blue.	Green.	Neutral Tint.	White.
43	60	80	75	0	6	37	100
44	74	88	80	4	14	41	100
45	90	90	90	7	22	43	100
46	96	84	80	12	28	43	100
47	94	70	40	16	34	40	100
48	90	50	16	21	40	39	100
49	80	40	10	26	44	39	100
50	66	30	6	32	46	40	100
51	52	22	5	41	40	40	100
52	40	17	4	51	32	40	100
53	38	13	4	56	24	38	100
54	35	10	3	59	17	35	100
55	32	6	3	60	13	32	100
56	31	3	2	57	10	29	100
57	31	2	2	53	8·5	27	100
58	30	1	2	50	8	25	100

From this table are deduced the luminosity curves which are in the following table, the luminosity curve of the white being that given in the Bakerian lecture for 1886.

Luminosity Curves.

Scale No.	Yellow.	Orange.	Red.	Blue.	Green.	Neutral Tint.	White.
43	1·5	2·0	1·8	0	1·2	·9	2·5
44	12·2	16·5	13·2	·6	2·3	6·7	16·5
45	58·5	58·5	58·5	4·5	14·3	28·0	65·0
46	90·2	79·0	75·2	11·2	26·3	40·4	94·0
47	94·0	70·0	40·0	16·0	34·0	40·0	100·0
48	84·6	47·0	15·0	19·7	37·6	36·7	94·0
49	64	32·0	8·0	20·8	35·2	31·2	80·0
50	28·7	13·0	2·6	13·9	20·2	17·4	43·5
51	10·0	4·4	·9	8·0	7·7	7·8	19·4
52	3·8	1·8	·4	4·9	3·0	3·8	9·6
53	2·0	·7	·3	3·2	1·4	2·2	5·8
54	1·2	·4	·2	2·1	·3	1·3	3·6
55	·7	·1	·1	1·2	·2	·7	2·1
56	·4	...	...	·7	·1	·4	1·3
57	·3	...	...	·5	·1	·3	1·0
58	·2	...	...	·3	...	·2	·6
Areas...	453	323	217	107	183	218	534

[The scale-numbers which apply to the Fraunhofer-lines are s follows :—A = 42·56, B = 43·34, C = 44·26, D = 46·54,] = 49·62, F = 52·08, G = 57·72.]

The areas of the curves are those shown in the table. Taking the area of the luminosity curve of white as 100, the following are the luminosities of the colours derived from the above :—

White.	Yellow.	Orange.	Red.	Blue.	Green.	Neutral Tint.
100	84	60	41	20	34	41

The readings by the new method were :—

White.	Yellow.	Orange.	Red.	Blue.	Green.	Neutral Tint.
77	65	45	31	15·5	27	31

Taking white as 100, as before, the readings reduce to :—

White.	Yellow.	Orange.	Red.	Blue.	Green.	Neutral Tint.
100	84	58	40	20	35	40

The exactitude of the latest method is again exemplified, but it is not pretended that it is quite so accurate as the older method.

The method described is particularly adapted to a coloured surface of small dimensions. Where, however, a circle of some 3 or 4 inches in diameter can be utilized, the following modification of Rood's method may be adopted. Behind the sectors and on the spindle of the rotating disks, a disk of white card can be placed. The sectors being blackened on the other side, when revolved we can produce any shade of grey from half black and half white to all black. On the other side of the sectors can be placed a smaller disk of coloured card, to be measured, and this will rotate with the sectors. Should the colour be a fairly dull one, the match of luminosity can be made by altering the shade of grey by rapid oscillation in aperture of the sectors, and the luminosity of the colour in terms of white determined when the amount of white light reflected from the black surface has been measured. Should the colour be more luminous than the grey given by half black and half white, the coloured disk can be toned down by means of a black semi-disk, adding a known quantity of the black surface by Maxwell's plan. The luminosities of the surfaces are then measured, and the true luminosity of the coloured surface in terms of the white surface, calculated after allowing for the added black.

This same plan may be adopted for measuring the *intensity* of the light of the various parts of the spectrum reflected from

a coloured surface, in comparison with that reflected from a white surface. Colour patches of monochromatic light are formed by the method given in the Philosophical Magazine for 1885 (vol. xx.), which fall on the coloured disk and the rotating sectors, which form a grey in white light. There is less difficulty in this case than in ascertaining the luminosity, as the colour falling on the mixture of black and white is the same as that falling on the pigment. In this case, too, it may be necessary to add a fixed amount of black to the coloured disk in order to get a reading.

In reply to questions, Capt. Abney said the spectrum-method was the more accurate and could be relied on to 1 per cent. The new method gave results within 2 per cent., showing that the eye is very sensitive to small changes of luminosity when such changes take place in rapid succession.

IX. *On the Suppressed Dimensions of Physical Quantities.* *By* A. W. Rücker, *M.A.*, *F.R.S.**

In the calculation of the dimensions of Physical quantities we not unfrequently arrive at indeterminate equations in which two or more unknowns are involved. In such cases an assumption has to be made, and in general that selected is that one of the quantities is an abstract number. In other words the dimensions of that quantity are *suppressed*.

The dimensions of dependent units which are afterwards deduced from this assumption are evidently artificial, in the sense that they do not necessarily indicate their true relations to length, mass, and time. They may serve to test whether the two sides of an equation are correct, but they do not indicate the mechanical nature of the derived units to which they are assigned. On this account they are often unintelligible.

Another difficulty is caused by the fact that the units which we find it convenient to use are sometimes themselves of an artificial character, and not such as would have been chosen had those who originally defined them possessed a clear conception of the nature of the phenomena with which they were dealing.

* Read November 24, 1888.

The obstacles which the study of the subject presents to students would, I think, be greatly reduced if in developing it symbols were retained in the formulæ to represent the quantities the dimensions of which are suppressed, and if the artificial appearance of the dimensions of many quantities were more clearly traced to the artificial character either of the quantities themselves or of the assumptions on which these dimensions are calculated.

It is probable that, as the mechanical explanation of physical phenomena proceeds, the use of units based on simple mechanical conceptions will be extended, that some quantities now employed will be dispensed with or regarded from a different point of view.

Thus the satisfactory expressions of the dimensions of the various thermal units is not possible so long as there is any doubt as to the mechanical definition of temperature.

The equation

$$[\mathrm{M\,L^2\,T^{-2}}] = [\mathrm{J\,M}c\theta]$$

leads, if we regard c as a number, to the result

$$[\mathrm{J}] = [\mathrm{L^2\,T^{-2}}\,\theta^{-1}].$$

The quantity θ can hardly be taken as an abstract number because the scale on which it is measured affects the numerical value of J, but, on the other hand, temperature as measured on the ordinary thermometer-scales has no relation to the units of length, mass, or time. No change in these units would affect the magnitude of the degree Centigrade or Fahrenheit. So long, therefore, as we adhere to the system of measuring heat in terms of calories instead of in ergs, temperature must be regarded as a fundamental quantity in the sense that the unit of temperature, though necessary for the expression of other thermal units, is itself independent of the units of length, mass, and time.

If it were sufficiently certain that the analogy offered by the theory of gases might be extended to all cases, it would follow that temperature depended only on mean energy of a particular kind (in gases the mean energy of translation possessed by the molecules. The mean value of a quantity is of the same dimensions as the quantity itself, and thus temperature might be regarded not only as being measured

by, but as being the mean energy of translation of a molecule, or of a standard number of molecules. The dimensions of temperature would thus be $[M L^2 T^{-2}]$. The number which expressed a given temperature would depend on the fundamental units, because they determine the magnitude of the unit of energy. It would be independent of the concrete mass or velocity of the molecules of any particular gas.

In the case of air at 0° C. and at atmospheric pressure V=48,500 centim. per second. If then, *exempli gratiâ*, the unit of temperature were that necessary to produce an increase of 1 erg in the mean total energy of translation of the number of molecules contained in 1 cub. centimetre of gas at 0° C. and at atmospheric pressure, the absolute temperature of melting ice on this scale would be

$$\tfrac{1}{2} \times \cdot 001293 \times 48500^2 = 1 \cdot 5207 \times 10^6.$$

Absolute temperatures Centigrade could be converted into this scale with considerable accuracy by the multiplier $10^5/18$; for, dividing $1 \cdot 5207 \times 10^6$ by this number, we get 273·7, which is the absolute temperature generally accepted as equivalent to 0° C. Heat absorbed by a gas at constant volume would be at once expressed in dynamical measure by the product of the change in temperature and of two abstract numbers, viz. the ratio of the number of molecules to the standard number, and the ratio of the increase of the total energy of a molecule to that of the energy of translation. Even if some such system should ultimately be adopted, our knowledge of the molecular construction and dynamics of solids and liquids is as yet too imperfect to warrant an attempt to place thermal units on a natural and mechanical basis. Until such a reform can be carried out, I think it would be best to place temperature in a class of *secondary fundamental units*, which, owing either to our ignorance or to our artificial methods of measurement, cannot be expressed in terms of length, mass, and time, and which must therefore be regarded as fundamental to other derived units which depend upon them.

The thermal units could then be tabulated in a more systematic manner than is usual, and the arbitrary character of the system would be emphasized by the symbol employed to

represent the dimensions of temperature. If θ be the symbol chosen, if specific heat be taken as a number, and the unit of heat be defined with reference to the unit mass of water, the following results are obtained :—

Quantity of heat	$[M\theta]$
Mechanical equivalent of heat	$[L^2 T^{-2} \theta^{-1}]$
Specific heat	1
Latent heat	$[\theta]$
Thermal capacity	$[M]$
Coefficients of expansion	$[\theta^{-1}]$
Coefficients of absorption and emission	$[ML^{-2} T^{-1}]$
Coefficient of conductivity	$[ML^{-1} T^{-1}]$
Entropy	$[M]$

Gravitation units hardly come within the scope of the present paper, but as they are important in their applications to thermal quantities I may indicate a method of dealing with them.

We must distinguish between the nominal unit of mass in such a system (M) and the real unit ($M\gamma$), where γ is the abstract number which expresses the acceleration of gravity in terms of the units of length and time. The three fundamental units in such a system are length, time, and force. Mass is a derived unit subject to the condition that $[L T^{-2}]$ is a given concrete acceleration. The only practically important cases are those of force, work, power, and the mechanical equivalent of heat, and if we multiply the number expressing any one of these quantities in a gravitation system by (the abstract number) γ, and remember the condition that $\gamma [L T^{-2}]$ is constant, transformations can be effected as usual.

Thus, if J, J′, and J″ be the numerical values of the mechanical equivalent expressed in an absolute, and two gravitational systems, we have

$$J [L^2 T^{-2} \theta^{-1}] = J' \gamma' [L'^2 T'^{-2} \theta'^{-1}] = J'' \gamma'' [L''^2 T''^{-2} \theta''^{-1}].$$

Thus to find the numerical value of J in the C.G.S. system when it is given in the English gravitational system,

$$J = 773{\cdot}2 \times 32{\cdot}2 \left(\frac{\text{foot}}{\text{centim.}}\right)^2 \left(\frac{\text{degree Cent.}}{\text{degree Fahr.}}\right) = 4{\cdot}16 \times 10^7.$$

To find J in the metre-kilogram-second gravitational system, when it is given in the British gravitational system, we reduce the last two of the above expressions by the relation $\gamma' [L' T'^{-2}] = \gamma'' [L'' T''^{-2}]$ to the form

$$J' [L' \theta'^{-1}] = J'' [L'' \theta''^{-1}];$$

so that

$$J = 773{\cdot}2 \left(\frac{\text{foot}}{\text{metre}}\right)\left(\frac{\text{degree Cent.}}{\text{degree Fahr.}}\right) = 424.$$

To reduce power from an absolute to a gravitational system, or *vice versâ*, we have

$$n_1 [M_1 L_1^2 T_1^{-3}] = n_2 [\gamma_2 M_2 L_2^2 T_2^{-3}].$$

Thus to find the number of ergs per second which correspond to one H.P.,

$$n = \frac{33000}{60} \times 32{\cdot}2 \left(\frac{\text{pound}}{\text{gram}}\right)\left(\frac{\text{foot}}{\text{cm.}}\right)^2 = 7{\cdot}46 \times 10^9.$$

It is noticeable that although the statement that J is independent of the unit of mass is in general true, it holds good only when the unit of heat and the unit of force are defined with respect to the same unit of mass. In a gravitational system this is not really the case, *e. g.* in the English system the unit of heat is defined with reference to the pound, while the employment of the gravitational measure of force involves a unit of mass = 32·2 lbs. Hence, even when the nominal unit of mass has disappeared, the number which expresses the ratio between the real and nominal units on the gravitational system remains in the expression for a quantity such as J, which is based upon others which have themselves involved the introduction of mass.

The open admission in the symbols employed that the dimensions of some of the quantities are unknown is more important in the case of the electrical and magnetic than in that of the thermal units.

As Maxwell showed, the independent relations between these quantities are one less than the number required to determine them completely. The electrostatic and electromagnetic systems are therefore deduced from assumptions which are equivalent to suppressing the dimensions of inductive capacity and magnetic permeability respectively. It would, I think, be better to retain in the tables of dimensions

symbols which represented these quantities as secondary fundamental units. The student would thus have brought more clearly before him the cause of the difference of the dimensions in the two systems, and the factors necessary to transform from the one system to the other would be indicated.

Thus if, instead of suppressing the dimensions of inductive capacity, we treat it as a secondary fundamental unit of unknown dimensions, we have the equations

$$[\mathfrak{D}\,\mathfrak{E}] = [\mathrm{M\,L^{-1}T^{-2}}], \quad [\mathfrak{D}] = [\mathrm{K}\,\mathfrak{E}];$$

whence

$$[\mathfrak{D}] = [\mathrm{M^{\frac{1}{2}}\,L^{-\frac{1}{2}}\,T^{-1}\,K^{\frac{1}{2}}}];$$

$$[\mathfrak{E}] = [\mathrm{M^{\frac{1}{2}}\,L^{-\frac{1}{2}}\,T^{-1}\,K^{-\frac{1}{2}}}].$$

In a precisely similar fashion we get

$$[\mathfrak{B}] = [\mathrm{M^{\frac{1}{2}}\,L^{-\frac{1}{2}}\,T^{-1}}\,\mu^{\frac{1}{2}}],$$

$$[\mathfrak{H}] = [\mathrm{M^{\frac{1}{2}}\,L^{-\frac{1}{2}}\,T^{-1}}\,\mu^{-\frac{1}{2}}].$$

By means of these relations all the units can be expressed in terms of M, L, T, K and M, L, T, μ, and the dimensions of M, L, T are those of the electrostatic and electromagnetic systems, according as the first or second mode of expression is adopted.

For since

$$[\mathfrak{D}] = [e\,\mathrm{L^{-2}}], \quad \therefore \quad [e] = [\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,K^{\frac{1}{2}}}];$$

and since

$$[\mathfrak{B}] = [m\mathrm{L^{-2}}], \quad \therefore \quad [m] = [\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}}\,\mu^{\frac{1}{2}}];$$

and from the dimensions of $[e]$ and $[m]$ those of all the other units can be found.

Maxwell has given a Table in which the dimensions of each of the electrical and magnetic units are expressed in terms of M, L, T, and of either electrical quantity or the strength of a magnetic pole. My suggestion amounts to nothing more than that we should use a similar list in which the unknown quantities are K and μ instead of e and m. The dimensions in terms of L, M, and T will then be those in the electrostatic and electromagnetic systems, and, instead of suppressing K and μ, we should retain them as representing dimensions which are unknown in terms of the fundamental units.

In cases where it is necessary to indicate whether the

quantity represented by a symbol is understood to be expressed in terms of K or μ, we may use the letters s and m subscript to distinguish between them. Thus e_s and e_m are not quantities whose dimensions are fundamentally different, but quantities the dimensions of which are unknown and are expressed in different ways in terms of other unknowns. The letters s and m indicate which of the two methods which are in practical use is employed.

By equating two such expressions for the same quantity, or by using any general relation between any two of the derived quantities, we get a necessary relation between the dimensions of the secondary fundamental units in terms of the primary fundamental units of length, mass, and time.

Thus we have from any one of Maxwell's equations (1) to (12) (p. 241) the general relations

$$[e\,m]=[\mathrm{M\,L^2\,T^{-1}}].$$

If we choose to express e in terms of K and m in terms of μ, the relation still obtains, and thus

$$[e\,m]=[\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,K^{\frac{1}{2}}}]\times[\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,\mu^{\frac{1}{2}}}]=[\mathrm{M\,L^2\,T^{-1}}];$$

$$\therefore\quad[\mathrm{K^{-\frac{1}{2}}\,\mu^{-\frac{1}{2}}}]=[\mathrm{L\,T^{-1}}].$$

It is obvious that there must be such a relation, for since only one equation is wanting for the complete determination of the dimensions in terms of L, M, and T, we cannot have two independent methods of expressing them.

If, then, we use the letters s and m subscript in the sense above explained,

$$[e_s\,m_m]=[\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,K^{\frac{1}{2}}}]\times[\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,\mu^{\frac{1}{2}}}],$$

$$[e_s\,m_s]=[\mathrm{M^{\frac{1}{2}}\,L^{\frac{3}{2}}\,T^{-1}\,K^{\frac{1}{2}}}]\times[\mathrm{M^{\frac{1}{2}}\,L^{\frac{1}{2}}\,K^{-\frac{1}{2}}}],$$

$$[e_m\,m_s]=[\mathrm{M^{\frac{1}{2}}\,L^{\frac{1}{2}}\,\mu^{-\frac{1}{2}}}]\times[\mathrm{M^{\frac{1}{2}}\,L^{\frac{1}{2}}\,K^{-\frac{1}{2}}}],$$

$$[e_m\,m_m]=[\mathrm{M^{\frac{1}{2}}\,L^{\frac{1}{2}}\,\mu^{-\frac{1}{2}}}]\times[\mathrm{M^{\frac{1}{2}}\,L^{\frac{1}{2}}\,T^{-1}\,\mu^{\frac{1}{2}}}];$$

and if we employ the relation

$$[\mathrm{K^{-\frac{1}{2}}\,\mu^{-\frac{1}{2}}}]=[\mathrm{L\,T^{-1}}],$$

we see that the right-hand sides of these expressions are all equal to each other and to $[\mathrm{M\,L^2\,T^{-1}}]$.

In this case the secondary fundamental units disappear from

the final expression. This would not always be the case for the product of any two units chosen haphazard, but it would always be true that any product or quotient of units could, by the relation

$$[K^{-\frac{1}{2}}\mu^{-\frac{1}{2}}]=[LT^{-1}],$$

be reduced to the same dimensions in terms of M, L, T, and either K or μ, whether they were or were not originally expressed in terms of one of these two last quantities only.

The method can be applied, not only to express more clearly that the absolute dimensions of the electrostatic and electromagnetic systems are the same, but to transform the numerical expressions for given concrete electrical or magnetic quantities from the one system of units to the other.

In order to transform a length from one scale to another by the relation $n_1[L_1]=n_2[L_2]$ we must know not only n_1 or n_2 but also the numerical value of the ratio L_1/L_2. In like manner, to transform electrical quantities from a system expressed in terms of K to a system expressed in terms of μ, we must know the numerical value of the ratio

$$K^{-\frac{1}{2}}\mu^{-\frac{1}{2}}/LT^{-1}.$$

If, then, v be the numerical value of the velocity of light expressed in terms of the units L and T, we can transform both dimensionally and numerically by the relation

$$[K^{-\frac{1}{2}}\mu^{-\frac{1}{2}}]=v[L\,T^{-1}].$$

Thus, to find the number of C.G.S. electrostatic units in y C.G.S. electromagnetic units of quantity, we have

$$x[L^{\frac{1}{2}}M^{\frac{1}{2}}T^{-1}K^{\frac{1}{2}}]=y\times[L^{\frac{1}{2}}M^{\frac{1}{2}}\mu^{-\frac{1}{2}}];$$

$$\therefore\quad x=y[L^{-1}TK^{-\frac{1}{2}}\mu^{-\frac{1}{2}}]$$

$$=y[L^{-1}T]\times v[LT^{-1}]=vy.$$

To find the number of C.G.S. Electromagnetic Units of Resistance in 20 C.G.S. Electrostatic units.

Working this out from first principles we have, by Maxwell's equations (*loc. cit.*) (2) and (4),

$$[R]=\frac{[E]}{[C]}=[M\,L^2\,T^{-1}\,e^{-2}];$$

whence, substituting for e in turn in terms of K and μ,

$$[R]=[L^{-1}TK^{-1}]=[LT^{-1}\mu].$$

Hence $$x[\mathrm{L T^{-1}}\mu] = 20[\mathrm{L^{-1} T K^{-1}}].$$

$$\therefore \quad x = 20[\mathrm{L^{-2} T^2 K^{-1}}\mu^{-1}].$$

And since $$[\mathrm{K^{-1}}\mu^{-1}] = v^2[\mathrm{L^2 T^{-2}}],$$

$$x = 20v^2,$$

which is correct.

In these cases the fundamental units of length, mass, and time, and the medium with respect to which the unit charge and the unit pole are defined, are the same in both systems of units; but the method can be extended to cases in which these conditions do not hold, and which are far more complex than those which are likely to occur in practice.

If the unit charge were defined to be such that two unit charges at a distance of 1 metre in a medium of which the inductive capacity was twice that of air, repelled each other with a force which would, in one second, produce in a centigram a velocity of 1 metre per second, we may find the number of ordinary electrostatic units to which it is equivalent. We have the general relation

$$x[\mathrm{L_1^{\frac{1}{2}} M_1^{\frac{1}{2}} T_1^{-1} K_1^{\frac{1}{2}}}] = 1 \times [\mathrm{L_2^{\frac{1}{2}} M_2^{\frac{1}{2}} T_2^{-1} K_2^{\frac{1}{2}}}];$$

$$\therefore \quad x = \left(\frac{\text{metre}}{\text{cm.}}\right)^{\frac{1}{2}} \left(\frac{\text{centigram}}{\text{gram}}\right)^{\frac{1}{2}} \left(\frac{\mathrm{K_2}}{\mathrm{K_1}}\right)^{\frac{1}{2}}$$

$$= 10^3 \times 10^{-1} \times \sqrt{2} = 100\sqrt{2}.$$

Thus if it were desired to find the number of C.G.S. electromagnetic units of charge in the unit electrostatic charge above defined, we should proceed as follows:—

$$x[\mathrm{L_1^{\frac{1}{2}} M_1^{\frac{1}{2}}}\mu_1^{-\frac{1}{2}}] = 1 \times [\mathrm{L_2^{\frac{1}{2}} M_2^{\frac{1}{2}} T_2^{-1} K_2^{\frac{1}{2}}}].$$

But $$\mu_1^{-\frac{1}{2}} = v_1 \mathrm{K_1^{\frac{1}{2}} L_1 T_1^{-1}};$$

$$\therefore \quad xv_1[\mathrm{L_1^{\frac{1}{2}} M_1^{\frac{1}{2}} T_1^{-1} K_1^{\frac{1}{2}}}] = 1 \times [\mathrm{L_2^{\frac{1}{2}} M_2^{\frac{1}{2}} T_2^{-1} K_2^{\frac{1}{2}}}];$$

where, as before, quantities with 2 subscript refer to the new unit. Of course v_1 must be expressed in terms of centimetres and seconds, as these are the magnitudes of $\mathrm{L_1}$ and $\mathrm{T_1}$ respectively.

$$\therefore \quad x \times 3 \times 10^{10} = 100\sqrt{2}, \qquad \therefore \quad x = \frac{\sqrt{2}}{3} \times 10^{-8}.$$

As a final example we may take the following problem, in which the data are chosen merely for the purpose of illustration:—Find the number of C.G.S. electrostatic units of

magnetic induction in 10 electromagnetic units of a system in which the units of length, mass, and time are the metre, centigram, and second respectively, and in which the specific inductive capacity and the refractive index of the standard medium with reference to air are 2 and 1·5 respectively. Assume that $K^{-\frac{1}{2}}\mu^{-\frac{1}{2}}$ is proportional to the velocity of light in the medium.

We have already seen that

$$[\mathfrak{B}] = [M^{\frac{1}{2}} L^{-\frac{1}{2}} T^{-1} \mu^{\frac{1}{2}}] = [M^{\frac{1}{2}} L^{-\frac{3}{2}} K^{-\frac{1}{2}}].$$

Hence if a subscript refers to air,

$$x\,[(\text{gram})^{\frac{1}{2}}(\text{cm.})^{-\frac{3}{2}} K_a^{-\frac{1}{2}}] = 10\,[(\text{centig.})^{\frac{1}{2}}\,(\text{metre})^{-\frac{1}{2}}\,(\text{sec.})^{-1}\,\mu^{\frac{1}{2}}].$$

We may now make the substitution

$$K_a^{-\frac{1}{2}} = 3\times 10^{10}\mu_a^{\frac{1}{2}}\,(\text{cm.})\,(\text{sec.})^{-1}$$

or else calculating the velocity of light in the medium from the refractive index, we may write

$$\mu^{\frac{1}{2}} = \frac{1\cdot 5}{3\times 10^{9}}\,K^{-\frac{1}{2}}\,(\text{metre})^{-1}\,(\text{sec.}).$$

By the first substitution we get

$$x\times 3\times 10^{10}\,[(\text{gram})^{\frac{1}{2}}\,(\text{cm.})^{-\frac{1}{2}}\,(\text{sec.})^{-1}\,\mu_a^{\frac{1}{2}}] = 10\,[(\text{centig.})^{\frac{1}{2}}\,(\text{metre})^{-\frac{1}{2}}\,(\text{sec.})^{-1}\,\mu^{\frac{1}{2}}];$$

$$\therefore\ x = \frac{10^{-9}}{3}\left(\frac{1}{10}\right)\times\left(\frac{1}{10}\right)\times\left(\frac{\mu}{\mu_a}\right)^{\frac{1}{2}} = \tfrac{1}{3}\times 10^{-11}\times 1\cdot 5\left(\frac{K_a}{K}\right)^{\frac{1}{2}} = \frac{1}{2\sqrt{2}}\times 10^{-11}.$$

By the second substitution,

$$x\,[(\text{gram})^{\frac{1}{2}}\,(\text{cm.})^{-\frac{3}{2}} K_a^{-\frac{1}{2}}] = 10\times\frac{1\cdot 5}{3\times 10^{8}}\,[(\text{centig.})^{\frac{1}{2}}\,(\text{metre})^{-\frac{3}{2}} K^{-\frac{1}{2}}]\ ;$$

$$\therefore\ x = \frac{1}{2\times 10^{7}}\left(\frac{1}{10}\right)\times\left(\frac{1}{100}\right)^{\frac{3}{2}}\left(\frac{K_a}{K}\right)^{\frac{1}{2}} = \frac{1}{2\sqrt{2}}\times 10^{-11}\ ;$$

which is the same result as before.

In such a problem the amount of time and thought saved by the method of dimensions extended to secondary fundamental units is considerable.

I think that these examples are sufficient to justify the change in the method of exhibiting the dimensions of electrical quantities which I advocate, apart from the great theoretical advantage of being able to write electrostatic and

electromagnetic quantities as being of the same absolute dimensions.

I therefore give a Table in which the powers in which K and μ enter into the various electrical and magnetic quantities are shown.

If we put $K=1$ we get the ordinary electrostatic, if $\mu=1$ the ordinary electromagnetic dimensions.

Table of Dimensions.

	Symbol.	Dimensions in terms of	
		L, M, T, and K.	L, M, T, and μ.
antity of electricity . . .	e	$[L^{\frac{3}{2}} M^{\frac{1}{2}} T^{-1} K^{\frac{1}{2}}]$	$[L^{\frac{3}{2}} M^{\frac{1}{2}} \mu^{-\frac{1}{2}}]$
ectric potential	E	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{-\frac{1}{2}}]$	$[L^{2} M^{\frac{1}{2}} T^{-1} \mu^{\frac{1}{2}}]$
antity of magnetism . .	m	$[L^{\frac{1}{2}} M^{\frac{1}{2}} K^{-\frac{1}{2}}]$	$[L^{\frac{3}{2}} M^{\frac{1}{2}} T^{-1} \mu^{\frac{1}{2}}]$
ectrokinetic momentum of a circuit	p		
ectric current	C	$[L^{\frac{3}{2}} M^{\frac{1}{2}} T^{-2} K^{\frac{1}{2}}]$	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-1} \mu^{-\frac{1}{2}}]$
agnetic potential . . .	Ω		
ectric displacement . .	$\mathfrak{D}$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{\frac{1}{2}}]$	$[L^{-\frac{3}{2}} M^{\frac{1}{2}} \mu^{-\frac{1}{2}}]$
rface density			
ectromotive force at a point .	$\mathfrak{E}$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{-\frac{1}{2}}]$	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-2} \mu^{\frac{1}{2}}]$
agnetic induction	$\mathfrak{B}$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} K^{-\frac{1}{2}}]$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} \mu^{\frac{1}{2}}]$
agnetic force	$\mathfrak{H}$	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-2} K^{\frac{1}{2}}]$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} \mu^{-\frac{1}{2}}]$
rength of current at a point .	$\mathfrak{C}$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-2} K^{\frac{1}{2}}]$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} \mu^{-\frac{1}{2}}]$
ector potential	$\mathfrak{A}$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} K^{-\frac{1}{2}}]$	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-1} \mu^{\frac{1}{2}}]$
pacity	$\left[\frac{e}{E}\right] = [\eta]$	$[LK]$	$[T^2 L^{-1} \mu^{-1}]$
efficient of self-induction .	$\left[\frac{p}{C}\right] = [L]$	$[L^{-1} T^2 K^{-1}]$	$[L\mu]$
ecific inductive capacity . .	$\left[\frac{\mathfrak{D}}{\mathfrak{F}}\right] = [K]$	$[K]$	$[L^{-2} T^2 \mu^{-1}]$
agnetic inductive capacity .	$\left[\frac{\mathfrak{B}}{\mathfrak{H}}\right] = [\mu]$	$[L^{-2} T^2 K^{-1}]$	$[\mu]$
sistance	$\left[\frac{E}{C}\right] = [R]$	$[L^{-1} T K^{-1}]$	$[L T^{-1} \mu]$
ecific resistance	$\left[\frac{\mathfrak{E}}{\mathfrak{C}}\right] = [r]$	$[T K^{-1}]$	$[L^2 T^{-1} \mu]$

To these we may add certain units in which both electrical and thermal quantities occur.

Thus, using the relations :—

Thermoelectric height × temperature = E.M.F.,

or Specific heat of electricity × temperature = E.M.F.,

$\Pi \times$ current × time = heat,

or $J\Pi$ = E.M.F.,

we get the following results :—

	Symbol.		
Thermoelectric height . .	kt	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{-\frac{1}{2}} \theta^{-1}]$	$[L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-2} \mu^{\frac{1}{2}} \theta^{-1}$
Specific heat of electricity			
Coefficient of Peltier effect	Π	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} T K^{-\frac{1}{2}} \theta]$	$[L^{-\frac{1}{2}} M^{\frac{1}{2}} \mu^{\frac{1}{2}} \theta]$
Geometrical capacity . .	$q' = \frac{q}{K}$	$[L]$	$[L]$

In conclusion, then, I think it would be well to introduce symbols for what I have called secondary fundamental units instead of suppressing their dimensions, for the following reasons :—

(1) We thereby generalize the method of determining by dimensional equations the relation between a change in the magnitude of the units and in the number of which a given quantity is expressed.

(2) In the case of the electrical and magnetic units the method indicates clearly the cause of the difference between the dimensions in terms of M, L, and T of the same quantity in the two systems.

(3) It indicates that the dimensions of different quantities in the same system, which are apparently the same with respect to M, L, T, really are or may be different, as their dimensions with respect to K or μ are different ;

$$e.g.\ [\mathfrak{D}] = [L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{\frac{1}{2}}]$$
$$[\mathfrak{E}] = [L^{-\frac{1}{2}} M^{\frac{1}{2}} T^{-1} K^{-\frac{1}{2}}].$$

(4) It suggests an explanation of the artificial and unintelligible character of the electric and magnetic units. If the dimensions of K and μ were known, they would probably be simplified.

(5) Lastly, I think the symbols are thus made to express the limits of our knowledge and ignorance on the subject more exactly than if we arbitrarily assume that some one of the quantities involved is an abstract number.

Mr. Blakesley, in commenting on thermal units, strongly protested against the use of the word "*Therm*" as a name for the unit of heat. If used at all, it should be reserved for the unit of temperature. Referring to the choice of fundamental units, he reminded the Society that the dimensions of quantity expressed in the electrostatic or electromagnetic systems become identical, if the unit velocity be the velocity of light; and by choosing the unit of time as a suitable decimal part of a day, the relations between electrical and practical mechanical units could be simplified.

Prof. Carey Foster, after discussing the effects of defining specific heat as a ratio, or as a quantity of heat on the dimensions of temperature, pointed out that as Quantity of heat = Temperature × Entropy, the dimensions of temperature would be determinate if those of Entropy were found.

Prof. S. P. Thompson considered part of the difficulties of dimensional equations arose from the fact that no distinction was made between *scalar* and *vector* quantities. Thus the dimensions of work and moment of a force are given as $\mathrm{M\,L^2\,T^{-2}}$, whereas the true representation for the latter would be $\mathrm{M\,L^2\,T^{-2}}\sqrt{-1}$, because the line by which the force is multiplied is at right angles to the force. By similar considerations, Ampère's rule for the force between two current elements can be derived from the magnetic equation $\frac{m\,m'}{r^2}=f$; for, replacing m and m' by equivalent current elements $i\,ds$ and $i\,ds'$, the equation becomes

$$f=\frac{\sqrt{-1}\,i\,ds\sqrt{-1}\,i\,ds'}{r^2}$$

$$=\frac{-i^2\,ds\,ds'}{r^2}.$$

Referring to the use of *Therm*, Dr. Thompson concurred with the remarks of Mr. Blakesley, and thought the word "*calorie*" answered all requirements. He also considered that

thermal equations were greatly simplified by always expressing specific heat in ergs.

Prof. Ayrton was of opinion that students experienced much greater difficulty in dealing with electrical units than with thermal ones, and thought part of this was due to the vague way in which some of the standard text-books treated the subject. With reference to the force exerted by quantities of electricity, Prof. Perry and himself had pointed out that specific inductive capacity must be taken into account, for, contrary to Faraday, they had found it to be different in different gases.

In reply, Prof. Rücker said he often explained the identity of the dimensions of work and moment of a force by considering moment as measured by the work done in rotating through unit angle, the dimensions of angle being zero as regards L, M, and T. He also pointed out that in Bayne's 'Thermodynamics' specific heats are always expressed in ergs.

In thanking Prof. Rücker for his interesting paper, the President expressed his conviction that, by paying attention to the points considered, the difficulties arising from the two systems of units would be considerably diminished.

X. *Note on a Modification of the Ordinary Method of Determining Electromagnetic Capacity.* *By* J. W. W. Waghorn, *D.Sc.**

The object of the proposed modification of the ordinary well-known method is to enable the capacity of a condenser or other conductor to be determined with sufficient accuracy without the costly apparatus generally employed.

The usual process consists, as is well known, in reading the "throw," d_1, of a galvanometer-needle under the impulse due to the flow of a quantity of electricity which charges the condenser to the potential of a certain battery, and in afterwards reading the steady deflexion, d_2 (not very different from d_1), when the galvanometer is connected in series through a total resistance R.

* Read December 8, 1888.

Then the required capacity, F (in farads) $= \frac{t \times d_1}{2\pi R d_2}$;

where t is the time of one complete vibration of the needle.

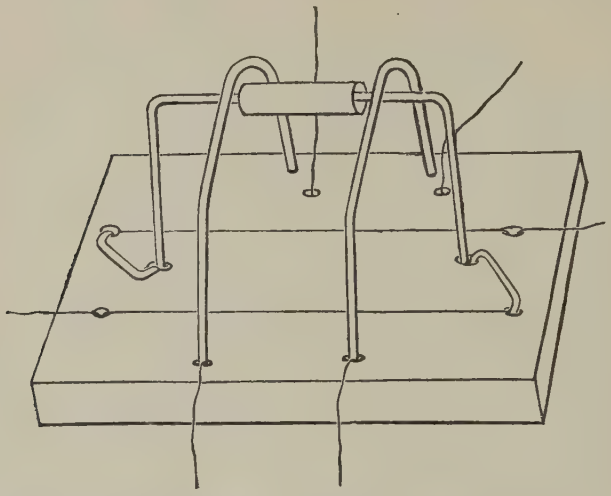
But as "damping" reduces the throw of the needle, the logarithmic decrement has to be determined and allowance made accordingly.

In attempting this determination of capacity with a sensitive galvanometer not specially designed for ballistic observations, the difficulties occur that in the first place the resistance, R, must be very great if d_1 is not to be very different from d_2; if the capacity of the condenser is $\frac{1}{2}$ microfarad, for example, and the time of vibration two seconds, the resistance required is more than 600,000 ohms, and these large resistances are not always available. Secondly, by reason of the shortness of the fibre suspension and its imperfect elasticity, the needle does not immediately take up its true position under the forces acting upon it, an imperfection which causes the deflexion due to the throw of the needle to be unfairly lessened in comparison with the steady deflexion against which it is compared; the final result being that in ordinary cases the capacity of the condenser may work out one, two, or even four per cent. less than its true value.

The first difficulty, the use of very high resistances, can be avoided, as suggested by Prof. Ayrton, by reducing the E.M.F. of the battery in a known ratio when obtaining the steady deflexion; but the second seems more troublesome to avoid, unless we are supplied generally with Mr. Vernon Boys's quartz fibres; but the difficulty may be turned if, instead of reading the permanent deflexion of the galvanometer, the throw on completing the circuit is read. This throw would, of course, if there were no damping, be double the permanent deflexion, and the damping need not be allowed for, since it is (at least very approximately) the same in the two observations made; that is, in the throw due to charging the condenser and also in the first elongation of the needle due to the alteration in the permanent field.

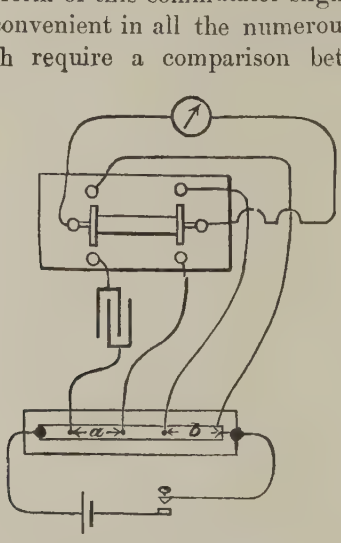
The requisite apparatus becomes then very simple, and such as is always likely to be at hand whenever such observations are required, and involves merely resistance-coils of, say, from 1 to 10,000 ohms with wandering leads, a sensitive galvano-

meter, and battery. A Pohl's commutator or rocking key is very convenient, but of course not indispensable, for com-



paring in rapid succession the two throws which form the actual experiment.

The ordinary form of this commutator slightly modified, as shown, is very convenient in all the numerous electrical observations which require a comparison between any two



deflexions, either steady or momentary, of an instrument such as a galvanometer or electrometer.

Let a be the resistance in that part of the resistance-coils between which the condenser circuit is applied, b the resistance in that part of the coils between which the permanent current is applied. The galvanometer itself forms a sufficient resistance to insert in the permanent-circuit branch, but its resistance must be known at the temperature at which it is used.

$$\text{F now} = \frac{t \times d_1 \times b}{\pi \times \text{G} \times d_2 \times a}.$$

The above expression is not strictly accurate, because damping occurs on an open circuit when the condenser is being charged, and on a closed circuit when the permanent current is flowing ; but in a galvanometer with any approach to ballistic properties the error may be considered as negligible for ordinary purposes ; for example, the logarithmic decrement of a galvanometer of 2000 ohms used in this operation on closed circuit was ·0428, on open circuit ·0415, involving an error of only one part in 2000, if the damping is entirely neglected in the two cases. With a Thomson galvanometer, in which the decrement reached the value of ·56 on open circuit, the error involved would, however, amount to one per cent.

The imperfect elasticity of the fibre may still exert a small influence, because the needle is swinging for a quarter period in the condenser charge and for a half period in the permanent-current observation; but if the error is not entirely obviated, it is brought down to very small limits.

Any sensitive galvanometer whose time of vibration exceeded two seconds, and in which there was not excessive damping, would probably be suitable for this determination ; if the period is too small, among other difficulties, that of self-induction, delaying the passage of the permanent current, would occur.

With the apparatus connected as shown to a galvanometer whose resistance is known, the actual determination need not take more than two or three minutes, and involves but very little more trouble than is necessary to determine the capacity in terms of a standard condenser, without reposing the confidence which is required in that case. With a galvanometer not specially chosen for the purpose, the capacity of a half

microfarad condenser, tested on several different occasions by different observers, gave ·497 for the lowest value and ·501 for the highest; but tested by the ordinary steady-deflexion method, the value determined was only ·485, the error in this case being due entirely to the imperfect elasticity of the short-fibre suspension.

The plan is not, however, suggested as a means of standardizing condensers where more refined means are available, but in the numerous cases where long-fibre ballistic galvanometers are not at hand and where an accuracy of, say, one half or one quarter per cent. is deemed sufficient.

Dr. Thompson pointed out that error frequently arises from the capacity of the key being appreciable where small condensers are being used, but the Author stated that the modification was not intended for such cases.

Prof. Ayrton remembered having used, in conjunction with Prof. Perry, the throw due to the permanent current instead of the steady deflexion, when experimenting with condensers containing E.M.F.s, and believed they abandoned it on account of the difference in decrement on closed and open circuits.

Mr. Sumpner regarded galvanometers with small differences in damping, on closed and open circuits, as unsuitable for ballistic purposes, and mentioned a case in which the latter was only half formed.

Mr. Boys considered the damping would be modified by having the condenser joined to the galvanometer-terminals, and thought the decrement should be decidedly different from that on pure open circuits.

In thanking the Author for his paper, the President said that any improved arrangements of known experiments or of lecture-apparatus would always be gladly received; and reminded members that in bringing such before the Society they would be carrying out one of the chief objects for which it was founded.

XI. *On some Facts connected with the Systems of Scientific Units of Measurement.* *By* T. H. Blakesley, *M.A., M.I.C.E.**

It seems to me a not unfitting opportunity, as a sequel to Prof. Rücker's suggestion, that we should modify some of our scientific formulæ, to inquire whether, with a change of formulation, we may not advantageously effect a change in some of the units themselves. That the C.G.S. and the practical system of units do not satisfy all the requirements of a perfect system of mechanical units must, I think, have occurred to others as well as to myself; and I mention this, not as an occasion for surprise, for indeed it would have been surprising if any system brought into vogue twenty years ago should still be found even to approach perfection, but rather in order to draw attention to the points in which these systems fail to give satisfaction, with a view to possibly rectifying their shortcomings.

The sense of imperfection may of course arise in the failure to attain to any one of the various ends which it should be the aim of a good system to reach.

I imagine that the following would be generally considered to be among those ends :—

First. All the quantities considered should be so connected by the equations representing the laws of nature, that no coefficients are required in expressing any units in terms of others. [Correlation.]

Secondly. Where quantities are recognized as being essentially of the same nature, they should be measured by the same unit. [Simplicity.]

Thirdly. Such a system should embrace all of the physical ideas which occur. [Comprehensiveness.]

Fourthly. Such a system should, so far as is compatible with other requirements, have its units closely and decimally connected with natural units. [Naturalness.]

Fifthly. The units should, subject to other considerations, agree with established though arbitrary units of measurement, actually or decimally. [Convenience.]

These five heads may be briefly described as:—

* Read December 8, 1888.

Correlation.
Simplicity
Comprehensiveness.
Naturalness.
Convenience.

I lay no particular stress upon the order in which these ends should be placed, though in my opinion the above order seems the true one, and I think most people would agree in putting Correlation at the top of the list. Its importance is so great that it has in fact been more completely realized than any of the others, most physical ideas having their due formulæ assigned and recognized. It has been the more easy to do this, since the process is absolutely independent of the real units employed. The ideas need only to have their physical nature truly comprehended.

In the second point—Simplicity—there has been much less progress made. In electrical matters, for instance, though in describing a magnitude it may be perfectly well understood what units of length, mass, and time form the fundamental basis of the measurement, it is further necessary to state whether the Electrostatic or the Electromagnetic system is contemplated.

Again, heat is recognized as a form of energy, and yet the two are not referred to the same unit. If they were so, Joule's equivalent would always be unity. The defects in Comprehensiveness have been lately discussed in this Society by Prof. Rücker*. The one with which I have been brought most in contact is the omission of temperature from the systems in use. I think that if generalizations as great as the Electromagnetic Theory of Light are to be made by the help of systems of units, the Thermometer ought at once to be brought in out of the cold region of unsympathetic isolation and independence.

In chemical physics are to be found some notable omissions in atomic heat and electrochemical equivalence. When we examine the units to note how many are founded upon natural magnitudes, we recognize that the second is not a subdecimal part of the solar day, but only the $\frac{1}{86400}$ of that natural unit. To set against this, however, it is a unit which is in common use.

* *Ante*, p. 37.

The centimetre is decimally connected with the earth's quadrant, and the unit of density is that of water, the gramme merely being derived from the centimetre and density of water by proper correlation.

In the quadrant-volt second, or practical system, the length unit is brought up to practical coincidence with the earth-quadrant; the second, as before, is the unit of time; and the other quantities are only decimally connected with the C.G.S. I am not aware that any accidental coincidences occur between other units of this system and natural ones, the nearest approach being probably the volt to the E.M.F. of a Daniell cell.

But it is when we compare the units with those of an arbitrary nature perhaps, but in common use, that the failure in actual coincidence or in decimal relation is most striking. The failure to introduce to any great extent the metrical measures of length into England as against the inch is a well-known case. Again, the horse-power and the erg per second are not decimally related.

So inconvenient is this last defect in the department of electromechanics, that Mr. Preece has suggested that engineers should give up the H.P. of James Watt and adopt in its stead 1000 watts. This suggestion has not, so far as I know, met with any support, perhaps because the modifications in the definition of the unit which would be necessary for its clear appreciation from a mechanical engineer's point of view have not been clearly stated. The evil implied in the suggestion is, however, great; and, if possible, something ought to be done to assuage the acute suffering which engineers feel in passing from H.P. to watts.

I think it will be conceded, too, that even the more hardened physicist feels some pangs of passage on the troubled sea of transformation from the *terra firma* of the Electrostatic system to that of the Electromagnetic; and I do not think a rapid answer could be given by many persons to the question, What is the value, in C.G.S. electrostatic units, of a current of (say) $33\cdot\dot{3}$ practical electromagnetic units? Yet in following out the experiments of Dr. Hertz, with which Mr. Tunzelmann has made us familiar, such a calculation must, I think, be made.

I will here give two formulæ, which will enable any magnitude given in one system to be brought into the other.

Let k = the exponent of l in electromagnetic system,
h = " " m " " "
n = " " l in electrostatic system,
q = " " m " " "
for any kind of magnitude brought into due correlation with others.

Then, to reduce between practical (quadrant-volt-second) units electromagnetic, and C.G.S. units electrostatic :

1 practical unit $= 3^{n-k}10^{10n-11q-k}$ electrostatic C.G.S.

To reduce between C.G.S. electromagnetic and C.G.S. electrostatic :

1 C.G.S. electromagnetic unit $= 3^{n-k}10^{10(n-k)+11(h-q)}$ electrostatic C.G.S. units.

The 3 in these equations is meant as a sufficient approximation to the number 2·998, which is one tenth of "v" in quadrants per second.

I have myself not seen such reduction-formulæ elsewhere, and under the present systems I think they may be found of use.

But it would be far better than employing such formulæ to have but one system for all measurements, and do away with this inconvenient bimetallism in the currency of science.

And in this case the way out of the difficulty is easy. We have only to adopt "v" as the unit of velocity. With this one restriction any magnitude will be expressed in a system based upon any units by the same number in either system. Such a system would be a veritable coalition, and for distinction might be so called.

A coalition system, then, merely requires that the unit of velocity shall be a certain one, which is also a natural one. It reduces the degrees of freedom in the choice of units by 1, and, without prejudice to Prof. Rücker's method of formulation, will allow us to fix almost any two other units arbitrarily. The two cannot of course be time and length, for velocity simply involves these alone. If the second were retained, the

unit of length would be 30 quadrants. If the quadrant were retained, the unit of time would be $\frac{1}{30}$ of a second.

If it be urged that a velocity of 30 quadrants per second is a large one, I would reply that it is only 30 times the present unit of velocity in the practical system ; and that experience shows that extremely high or low units do not materially affect calculations. The unit of capacity is a million times the microfarad of our laboratories, and that of velocity about a million times the speed of an express-train. The use of mega- and micro- has now been found by experience to present no difficulty or objection.

Thus this change in the unit of velocity would not introduce inconvenience in itself; but unfortunately, since $v = \frac{l}{t}$, its change would necessitate one indirectly in either length or time, and clocks and meters are so commonly in use that any interference in their present constructions would be felt a serious thing. Of the two changes, that of the time unit seems to me simplest. To take $\frac{1}{30}$ of a thing which itself is $\frac{1}{60}$ of a minute, that again being $\frac{1}{60}$ of an hour, does not appear so very radical an operation.

If we calculate the various units obtained by this change in the time unit and compare them with the quadrant-volt-second units, we shall find (column V.) that mass, length, and quantity of electricity remain unaltered ; time and conductivity become $\frac{1}{30}$; velocity, momentum, current, resistance, magnetic field, pole, and magnetic moment, 30 times ; force, acceleration, energy, and E.M.F., 900 ; and power, 27,000 times of the practical units ; while capacity sinks to $\frac{1}{900}$ of a farad.

This would, however, leave the connexion between the unit of power and 1 horse-power bad, for 1 unit would be about 36·2 H.P.

The correlation of temperature with other units would be, I imagine, best effected by the definition that a unit-of-temperature change shall be that through which a unit of energy in the form of heat would raise a unit of matter possessing unit specific heat ; in other words, the equation

$$ml^2t^{-2} = \mathrm{J}mc\theta$$

should be satisfied by $\mathrm{J} = 1$.

Since heat is recognized as energy, J must be numerical, notwithstanding arguments have been adduced against this view. It is sometimes said that J cannot be numerical because it changes with a change of units. This only arises from the fact that heat in the form $mc\theta$ is not properly correlated, because $(c\theta)$ is not so. Those who use this argument should apply it in some other case, when the fallacy would be apparent; *e. g.*

Power in watts $=746$ horse-powers,

Power in ergs per sec. $=10^7 \times 746$ horse-powers.

Here the factor has changed with a change of units, but no one would deny its being numerical, or the relation of one magnitude to another of the same nature.

If therefore J is reduced to unity by the above definition, we have $(c\theta)=l^2t^{-2}$ for the dimensions of temperature $\times$ specific heat; and if c is taken as numerical, these become the dimensions of θ.

As regards the relation between a degree so obtained and a thermometer-degree, we have the following facts to go upon:—

$4{\cdot}2 \times 10^7$ ergs raise 1 gram of water 1° C.,

$\therefore$ 1 erg raises 1 gram of water through $\left(\frac{1}{4{\cdot}2 \times 10^7}\right)^\circ$ C.

$\therefore$ 1° C. $= 4{\cdot}2 \times 10^7$ degrees C.G.S. (water).

1° F. $= 2{\cdot}3 \times 10^7$ „ „ „

1° R. $= 5{\cdot}25 \times 10^7$ „ „ „

These degrees therefore do not fit in decimally with the arbitrary scales in use.

But the number 4·2 may be written $\frac{1}{{\cdot}2381}$. If therefore we use as the standard of specific heat a substance which, referred to water, will have the specific heat ·2381, we shall then have

1° C. $=10^7$ C.G.S. (substance in question).

Now Regnault's value for specific heat of air at constant pressure is ·2375, Wiedemann's value is ·2389. The mean of these is ·2382.

If therefore we adopt the specific heat of air at constant pressure as the standard of specific heat, we have

1° C. $=10^7$ of 1 C.G.S. (air) unit.

The practical unit would be 10^{18} of a C.G.S. unit, and therefore would be 10^{11} of a degree Centigrade.

In relation to the thermometer, air has other well-known advantages over liquids, and is already the standard for specific inductive capacity and magnetic permeability.

This decimal relation of the Centigrade thermometer would not exist if the coalition of the Electromagnetic and Electrostatic systems were carried out on the lines I have indicated, viz. by making $\frac{1}{30}$ of a second the unit of time. The new unit of temperature would then be 900 times that of the electromagnetic quadrant-volt-second air unit.

Hence

1 unit of temperature $= 900 \times 10^{11}$ of 1 degree Centigrade.
" " $= 1620 \times 10^{11}$ " Fahrenheit.
" " $= 720 \times 10^{11}$ " Réaumur.

The endeavour to bring the horse-power and the unit of power into decimal relation may be guided by throwing the formulæ into terms of length, time, and power; and I have accordingly given a table of the ideas involved on this basis, in column VII. Any magnitude which appears in these formulæ unencumbered by the symbol of power will of course be unaltered by a mere change in its unit. Hence, if we adopted as the unit of power, ·746 of the watt or a decimal multiple of that quantity of power, we could bring the unit of power into decimal relation with the horse-power without altering the units in the practical system of time, length, velocity, acceleration, resistance and conductivity, and capacity. Thus the expensive standards of our laboratories, of resistance and capacity, our resistance-boxes and our microfarads, would remain to us. But our boxes of grammes would fall in value. The unit of temperature, however, would not be altered, so that Centigrade thermometers would remain. Column VIII. expresses the results of such a change.

No doubt if we did not suffer from an hereditary duodecimal taint, we might discard the $\frac{1}{86400}$ of a day, called a second, and adopt the $\frac{1}{100000}$ of a day as our unit of time, and that interval would be ·864 of a second, which number

happens to be the square root of ·746; and this would give us a coincidence in magnetic field, whose formula is $v^{-\frac{3}{2}} t^{-1} p^{\frac{1}{2}}$. But magnetic field is not a magnitude of which we keep instrumental standards, as we are wont to do of resistance, capacity, mass, time, length, and sometimes of E.M.F.

It will be observed that in the formulæ the symbol of power occurs either simply or raised to the power of $\frac{1}{2}$, and we may bring power into decimal relation with horse-power either by taking ·746 of the unit or 7·46. The square roots of these relations are ·86373 and 2·73136. Using the latter number we should obtain no further coincidences among the magnitudes.

In reviewing the results indicated by the above calculations, in dealing with the units of science in such a way as to obtain :—

(1) The correlation of the thermometer ;

(2) The unity of the two systems, Electrostatic and Electromagnetic ;

(3) The bringing of the unit of power into decimal relation with the horse-power ;

I come to the conclusion:—

(1) The thermometer Centigrade may be brought into decimal relation with temperature-units on the C.G.S. system or quadrant-volt-second system by adopting the specific heat of air at constant pressure as unity.

(2) That such decimal relation is compatible with a change in the unit of power to $\frac{1}{1000}$ of 1 H.P., which latter change could take place without changes in the units of time, length, velocity, resistance, and capacity, but would involve a change in the important standards of mass.

(3) That the union of the two electrical systems could be brought about in the simplest way by taking $\frac{1}{30}$ of one second as the unit of time ; such a change retaining the gramme-boxes, and the metre decimally, and the coulomb, but requiring the unit of capacity to be $\frac{1}{900}$ of 1 farad and the unit of resistance to be 30 ohms.

To my mind the last change recommends itself. No real change would be necessary in the face of the chronometer, or in the metre, or in the gramme-boxes. Each microfarad would have to be called ·0009, and each second 30, and every

Mechanical and Electromechanical Units.

I. Electrostatic formula in l, t, m.	II. Idea.	III. Electromagnetic formula in l, t, m.	IV. Practical Units in terms of C.G.S. Electromagnetic.	V. Coalition Units. Quadrant, $\frac{1}{3\cdot0}$", $\frac{\text{gramme}}{10^{11}}$ in terms of Practical Units.	VI. Coalition Units, as in V., in terms of C.G.S. Electrostatic Units.	VII. Electromagnetic formula in l, t, and p (power).	VIII. Electromagnetic Units. Quadrant, Second, ·746 Watt, in terms of Practical Units.	IX. Electromagnetic Units. Quadrant, Second, 7·46 Watts, in terms of Practical Units.	X. Coalition system. Quadrant, $\frac{1}{3\cdot0}$", ·746 Watt, in terms of Practical Units.
	Time.	t	1	$\frac{1}{3\cdot0}$		t	1	1	$\frac{1}{3\cdot0}$
	Mass.	m	10^{-11}	1		$l^{-2}\ t^{3}\ p$	·746	7·46	·0000276
	Length.	l	10^{9}	1		l	1	1	1
	Velocity.	$l\ t^{-1}$	10^{9}	30		$l\ t^{-1}$	1	1	30
	Force.	$l\ t^{-2}\ m$	10^{-2}	900		$l^{-1}\ t\ p$	·746	7·46	·02487
	Acceleration.	$l\ t^{-2}$	10^{9}	900		$l\ t^{-2}$	1	1	900
	Momentum.	$l\ t^{-1}\ m$	10^{-2}	30		$l^{-1}\ t^{2}\ p$	·746	7·46	·008289
	Energy.	$l^{2}\ t^{-2}\ m$	10^{7}	900		$t\ p$	·746	7·46	·02487
	Power.	$l^{2}\ t^{-3}\ m$	10^{7}	27000		p	·746	7·46	·746
$l^{\frac{3}{2}}$ t^{-1} $m^{\frac{1}{2}}$	E.M.F.	$l^{\frac{3}{2}}\ t^{-2}\ m^{\frac{1}{2}}$	10^{8}	900	3	$l^{\frac{1}{2}}\ t^{-\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	4·731
$l^{\frac{3}{2}}$ t^{-2} $m^{\frac{1}{2}}$	Current.	$l^{\frac{1}{2}}\ t^{-1}\ m^{\frac{1}{2}}$	10^{-1}	30	9×10^{10}	$l^{-\frac{1}{2}}\ t^{\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	·1577
l^{-1} t	Resistance.	$l\ t^{-1}$	10^{9}	30	$\frac{1}{9}10^{-9}$	$l\ t^{-1}$	1	1	30
l t^{-1}	Conductivity.	$l^{-1}\ t$	10^{-9}	$\frac{1}{3\cdot0}$	30×10^{9}	$l^{-1}\ t$	1	1	$\frac{1}{3\cdot0}$
$l^{\frac{1}{2}}$ t^{-1} $m^{\frac{1}{2}}$	Quantity.	$l^{\frac{1}{2}}\ m^{\frac{1}{2}}$	10^{-1}	1	3×10^{9}	$l^{-\frac{1}{2}}\ t^{\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	·00526
l	Capacity.	$l^{-1}\ t^{2}$	10^{-9}	$\frac{1}{9}\frac{1}{0}\frac{1}{0}$	10^{9}	$l^{-1}\ t^{2}$	1	1	$\frac{1}{9}\frac{1}{0}\frac{1}{0}$
$l^{\frac{1}{2}}$ t^{-2} $m^{\frac{1}{2}}$	Magnetic field.	$l^{-\frac{1}{2}}\ t^{-1}\ m^{\frac{1}{2}}$	10^{-10}	30	90	$l^{-\frac{3}{2}}\ t^{\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	·1577
$l^{\frac{1}{2}}$ $m^{\frac{1}{2}}$	Pole.	$l^{\frac{3}{2}}\ t^{-1}\ m^{\frac{1}{2}}$	10^{8}	30	10^{-1}	$l^{\frac{1}{2}}\ t^{\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	·1577
$l^{\frac{3}{2}}$ $m^{\frac{1}{2}}$	Magnetic moment.	$l^{\frac{5}{2}}\ t^{-1}\ m^{\frac{1}{2}}$	10^{17}	30	10^{8}	$l^{\frac{3}{2}}\ t^{\frac{1}{2}}\ p^{\frac{1}{2}}$	·864	2·731	·1577
	Temperature.	$l^{2}\ t^{-2}$	10^{18}	900		$l^{2}\ t^{-2}$	1	1	900

30 ohms 1 unit. A habit has arisen of attaching particular names to units. This, without doing very much good, adds greatly to the stability of the unit, and makes any subsequent change so much the more difficult. The practice has almost always been confined to electricians, somewhat too oblivious of the mechanical basis of a proper system.

Sir William Thomson, in a paper on units of measurement, contemplates a time when many of the units we now employ will become things of the past by the introduction of the universal gravitation method of connecting mass with length and force.

The naming of particular units employed for a time in the process of this development cannot but retard its progress, and the unity of science should take place independently of the subdivisions which may exist to-day.

It is highly probable that chemical science may soon require a modification of our present units, and we must not keep combining weights, atomic heat, and so on, uncorrelated with the rest of the body of science because the development of science has taken the order it has done. It might have been quite otherwise.

Dr. Whewell entertained a speculation as to whether the laws of motion would ever have been discovered by an intellectual race of jelly-fish inhabiting a world in which were no solid bodies.

In like manner we may imagine that had Torpedoes, or other animals armed with a controllable electrical equipment, won the race for supremacy against man, the laws of electricity might have been reached before the mechanical laws. Faraday and Maxwell would have preceded Galileo and Newton, and Gymnotus might have exhibited in submarine air-cases that uncanny biped Homo who could give you a curious and mysterious shock with a stick or a stone.

Prof. Rücker expressed his opinion that temperature would be best correlated by expressing it as energy, instead of making its dimensions $l^2 k^{-2}$ as suggested in the paper.

Dr. S. P. Thompson thanked the Author for his prefix "*megisto*," denoting "multiply by 10^{12}." Referring to the choice of air as the standard for specific heat, he remarked

that convenient coincidences were not always to be trusted, and that the specific heat of air depended on the pressure to which it was subjected.

XII. *On a Method of Comparing very unequal Capacities.* *By* Mr. H. Fison, *D.Sc.**

(Abstract.)

One coating of each condenser is joined to earth and to one end A of a high resistance (20,000 or 30,000 ohms) through which a current is flowing. The small condenser is charged to the P.D. existing between the ends A, B of the resistance and discharged into the large one. This is repeated a great number of times. If C be a point between A and B, the resistance between A and C may be varied until the P.D. between them is equal to that between the coatings of the condensers after n operations. If the insulated coatings be now joined to C through a galvanometer no deflexion will result. The relation between the capacities C_1 and C_2 of the large and small condensers is given by

$$\left(1+\frac{C_2}{C_1}\right)^m = \frac{R_{AB}}{R_{BC}},$$

where R_{AB}, R_{BC} are the resistances between AB and BC respectively.

Since time is required to prepare the operations the instantaneous capacities cannot be compared, and accordingly the measurements are taken after a definite time of electrification. A special rotating key was shown for performing ten operations per revolution, in which a trigger arrangement was provided for stopping the rotation after a predetermined integral number of revolutions. The method has been used for comparing a small air-condenser with a microfarad. The capacity of the former was also calculated electrostatically (correction being made for the edges), and that of the latter measured electro-magnetically by a ballistic galvanometer.

* Read June 9, 1888.

The results give a value for v equal to $2{\cdot}965 \times 10^{10}$. In these experiments the capacity of the rotating key was allowed for. Under favourable conditions, capacities in the ratio of 1 to 1000 or 1 to 10,000 can be compared with an accuracy of $\frac{1}{4}$ per cent.

Prof. Ayrton thought the novelty of the arrangement was in the rotating key, as the method of comparing unequal capacities by charging the smaller and discharging it into the larger a considerable number of times had been described and used by himself and Prof. Perry in their experiments on the Specific Inductive Capacity of Gases.

XIII. *On the Divergence of Electromotive Forces from Thermochemical Data.* *By* E. F. Herroun, *Professor of Natural Philosophy in Queen's College, and Demonstrator in King's College, London**.

The fact that with many voltaic cells the electromotive forces observed experimentally do not accord with values calculated from the thermochemical equations representing the reactions occurring within the cells, has been the subject of remark by several investigators, including Favre, Julius Thomsen, Braun, Helmholtz, Willard Gibbs, Wright and Thompson, and others. But although, at the present time, we are in possession of a knowledge of the actual and computed values of the electromotive forces of a large number of voltaic cells, anything approaching a complete explanation of the reason why certain cells should give electromotive forces in excess, others in defect, others again according almost exactly with the calculable values, is still wanting.

It was in the hope of deciding certain questions and of going some way on the road to a final solution of the problem that the present research was undertaken.

Certain cells, like the 'Grove' or 'Bunsen,' in which nitric acid is reduced by the evolved hydrogen, are said to furnish, with nitric acid of certain degrees of concentration, electromotive forces somewhat in excess of the values calculated from the thermal effects accompanying the chemical changes;

* Read January 26, 1889.

but the effect of solution of the oxides of nitrogen or their evolution as gas, together with other effects of dilution of the acid, complicate the subject from the theoretical standpoint, and their non-reversibility renders them unsuited for experiment. Cells of the Daniell type are therefore greatly to be preferred, both for theoretical consideration and direct experiment.

Thanks to the careful and accurate data furnished by the published researches of Dr. C. R. A. Wright and Mr. C. Thompson, and their clearly tabulated results*, one can see at a glance whether the electromotive force furnished by two metals immersed in solutions of their corresponding salts accords with, exceeds, or falls below the value calculated from thermochemical data, and the exact amount of the discrepancy.

The explanations which might be given of the cause of the departure of observed E.M.F.s from the calculated values in different cells may be classified under the following heads:—

1. Certain cells in which the anticipated chemical change does not occur, but some other, different, reaction which evolves heat, to an extent which would account for the observed E.M.F. This is brought about by the special behaviour of a metal surface, and probably depends upon—

2. The coating of a metal surface by films of oxide or subsalts either more or less readily reduced than the normal salt of that metal.

3. The effect of dissolved gases, notably oxygen, in the solutions of the metallic salts.

4. The hydration or solution of the salts formed in some cases, but not in all, supplementing or diminishing the E.M.F. due to the reaction of the solid salts.

5. The evolution or absorption of sensible heat in the cell, and the loss or gain in electric energy, corresponding thereto.

In illustration of case 1 may be mentioned a cell consisting of aluminium in aluminic sulphate opposed to zinc in zinc sulphate, in which the thermochemical data would indicate

* "The Determination of Chemical Affinity in terms of Electromotive Force," pt. ix., Proc. Phys. Soc. vol. vi. pt. iv., and Phil. Mag. ser. 5, vol. xix. No. 118.

that aluminium would be the metal attacked, giving, when opposed to zinc, an E.M.F. of about 1 volt; whereas, in practice, zinc is the metal which is attacked, and the cell furnishes an E.M.F. of about ·53 volt. But we know that the chemical reaction $Al_2(SO_4)_3 + Zn_3 = 3(ZnSO_4) + Al_2$ does not occur, so that the aluminium plate merely acts as an imperfect substitute for an entirely non-attackable substance such as platinum or carbon, and having *hydrogen*, not aluminium, deposited on its surface.

That this is the case, and that the reason is probably to be found in the superficial coating of the aluminium plate by an oxide or suboxide, has been already put forward and received experimental verification by Dr. A. P. Laurie*, who has investigated the effect of amalgamating the aluminium, which better enables it to come in actual contact with the liquid and causes the E.M.F. of the cell to actually reverse in direction.

The heat developed by the oxidation or conversion into sulphate of the zinc with the liberation of hydrogen would be more than sufficient to account for the observed electromotive force; hence if it be desired to trace any connexion between the absorption or evolution of heat and the anomalous E.M.F. of any cell, it is the actual chemical change that does occur which must be made the basis of the calculation. Further, the term "*Thermovoltaic Constant*" (employed by Messrs. Wright and Thompson to denote the extent of departure of the E.M.F. of a cell from thermochemical data; zinc being taken as the standard from which the voltage is reckoned) in cases such as aluminium can merely express the fact that a plate of aluminium in its compact form, and probably covered by its protecting film of oxide, is less actively attacked than it ought to be from theoretical consideration of the heat of formation of its salts; but it must not be accepted as denoting any occult power of transforming electric energy into heat or *vice versâ*.

From purely *à priori* considerations one would expect that metals like aluminium and magnesium, which in the amalgamated or finely divided condition readily decompose water, would, in the compact form, become covered superficially with oxide and behave to a greater or less extent as a

* Phil. Mag. ser. 5, vol. xxii. p. 213.

hydrogen plate. It is therefore largely to this cause that one would look for an explanation of the large + values assigned to the "thermovoltaic constants" of aluminium, magnesium, and possibly iron. The observation by Wright and Thompson, that the substitution of dilute sulphuric acid for ferrous sulphate as the liquid surrounding the iron plate of an iron-copper cell uniformly tends to *lower* the E.M.F., which effect they refer to "local action," distinctly supports the view that even with iron there is a tendency to decompose water and coat itself with hydrogen, and thus acquire a higher relative potential.

A further consideration of case 2 will be met with later in this paper. I will merely mention that a considerable difference in E.M.F. due to the superficial coating of a copper plate with suboxide has been already noticed in the use of standard Daniell cells by Dr. J. A. Fleming * and myself †, and that what is rare and comparatively unimportant in the case of copper may become the rule and of greater importance in some other combinations.

In case 3 the nature of the effects of dissolved oxygen in oxidizing a metallic surface or in removing traces of electrolytic hydrogen and its depolarizing effect in the latter case are too obvious to need much comment; only I would draw attention to the fact that by its action the electromotive force on open circuit, as measured by an electrometer, or with a balance of difference of potential, as in Latimer Clark's method, or even when measured by a galvanometer of many thousand ohms resistance, is liable to be in excess of that due to the supposed chemical reaction, and therefore to give false ideas as to the energy-producing power of the cell.

Case 4 has been suggested as a very probable source of divergence, since (1) in cells in which a very sparingly soluble salt is employed, the solution, especially in the vicinity of the electrode, may become saturated, and if any more salt be formed it will necessarily be produced in the solid form, which may, or may not, be dissolved in the rest of the liquid; (2) it is difficult to see how the tendency of a salt to combine molecularly with water to form a hydrate or to dissolve as a

* Phil. Mag. ser. 5, vol. xx. p. 132; Proc. Phys. Soc. vol. vii. p. 168.

† Phil. Mag. ser. 5, vol. xxi. p. 12; Proc. Phys. Soc. vol. vii. p. 276.

solution, can directly affect the combination of the metal with the acid radical to form that salt, and therefore we may be justified in concluding that both the total heat evolved and the E.M.F. of a cell are due to the algebraic sum of effects of events which take place successively. But since the water in different solutions is differently combined or related with the anhydrous salt, it appears possible that the energy which in some cases is transformable into electric energy, or, to use Helmholtz's suggestive names, is "free," in other cases may be simply "bound energy."

The main interest of the question, however, centres in case 5, since many physicists seem to have tacitly assumed that the explanation of the divergence of actual E.M.F.s from the computed values is simply that with cells giving a deficiency of electromotive force a portion of the chemical energy appears as heat in the cell, while cells giving an excessive electromotive force are spoken of as doing so "at the expense of sensible heat." They have not, however, given any reason for such differences of action, and they do not appear to have considered all the consequences which the adoption of the latter part of this view would entail.

Helmholtz, in his papers "Zur Thermodynamik chemischer Vorgänge,"* suggests the treatment of a voltaic cell as a reversible thermodynamical process, and that the nature of its working may be detected by the difference of E.M.F. brought about by change of temperature. The cell selected for examination is his zinc-mercurous chloride battery, the E.M.F. of which is very slightly increased by rise of temperature; and the chief discussion is the relation of the vapour-tension of the zinc-chloride solution, the "free energy of the salts," and the electromotive force dependent on differences of concentration.

But that part of his conclusion in which he states that "*the electromotive force between the metals increases with heating*, i. e. *the calomel battery belongs, as I have already mentioned, to the batteries which fix heat, which in part work at the expense of the thermometric heat of surrounding bodies*," is based either purely on thermochemical data or without due consideration

* *Sitzungsbericht. d. Akad. d. Wissenschaft. zu Berlin.* Translated and pub. in Physical Memoirs, by the Phys. Society, vol. i. pt. 1.

of what the adoption of that view would entail in the case of the strictly comparable zinc-mercurous sulphate cell of Latimer Clark, which decreases in E.M.F. by a considerable proportion as its temperature is raised, although this also is a cell giving an E.M.F. in excess of the supposed thermochemical effect.

Now viewing a cell as a strictly reversible thermic engine, if a portion of its E.M.F. be due to the absorption of sensible heat, then, when worked backwards, an exactly equivalent amount of heat would be evolved in the cell. Therefore, taking two Latimer Clark cells, joined by their like poles, one at a high, the other at a low relative temperature, the one at the low temperature having the higher E.M.F. will send a current against the E.M.F. of the one at the higher temperature.

But the current through the cold one will be direct, while that through the warm one will be inverse, so that heat will be absorbed in the cell at low temperature and evolved in the cell at high temperature; and since for unit quantity of electricity flowing the same amount of chemical work will be performed in each cell, but reversed in one, we should have an instance of a thermodynamical arrangement working by means of a difference of temperature, the effect of which would be to cool the cold cell and heat the hot one; or heat would be transferred from the cold to the hot body, and be made capable of performing mechanical work, instead of requiring its expenditure. It does not appear to me that this could be adequately explained by the different heats of dilution of the salt at different temperatures, so that the result of believing that a Latimer Clark cell works partly "at the expense of sensible heat" is a direct contradiction of the principle of the second law of thermodynamics, as this would require that its E.M.F. should rise with rise of temperature. That it is the postulate with regard to mercury cells, and not the second law, which is fallacious, I hope to show later in this paper.

If two plates of zinc, one amalgamated and the other plain, be immersed in a solution of zinc sulphate, on completing the external circuit a current is found to flow from the amalgamated to the non-amalgamated plate through the cell;

but Prof. J. Willard Gibbs in his paper "On the Equilibrium of Heterogeneous Substances,"* remarks that such a current could not have the effect of dissolving zinc from the amalgamated plate and depositing it on the non-amalgamated plate, as this deposited zinc might be immediately redissolved in mercury to form an amalgam with merely the absorption of sensible heat.

By the use of pure zinc foil in solutions of zinc sulphate, free from oxygen, I have found that the difference of potential between amalgamated and plain zinc becomes exceedingly small; and in the case of a cell freely exposed to air the current on a circuit of only 1·5 ohm's resistance did not deposit any weighable quantity of zinc on the plain zinc electrode after passing for seven days. This, therefore, is in confirmation of the theoretical conclusion from the second law put forward by Willard Gibbs, and renders it more imperative to stringently examine any reputed case of the production of electrical energy at the expense of thermometric heat.

It therefore became important to examine on an experimental basis the theory that reversible heat effects are associated with cells giving anomalous electromotive forces.

Method.

The method usually adopted may be briefly described as follows:—The experimental cell was constructed of a thin glass beaker as the outer vessel, containing one of the metal electrodes in a solution of one of its salts, and a porous earthenware cell, which contained the other metal in a solution of its corresponding salt. Cells of the Raoult form could not be employed on account of their inconvenience for thermal measurements and their necessarily high internal resistance. Attempts to reduce resistance by substituting animal membrane, parchment-paper &c. for the porous cell were abandoned owing to the facility with which they allowed small but significant quantities of the solutions to mingle by diffusion, and so permit the deposition of one metal on the more electropositive one, generating local heat and altering

* Trans. Connect. Acad. vol. iii. pts. 1 and 2.

the electrical constants. The cell was supported by the rim of the beaker resting on a cork edge which was fitted into the top of a tin cylinder, the latter being itself suspended within a larger cylinder of bright tin. With this apparatus, when containing the usual working quantities of solutions, the rate of loss of heat was equal to $\frac{1}{100}$ of a gram-degree Centigrade for each minute-degree above the surrounding air temperature, for the few degrees of the experimental range.

Thermometers graduated to fractions of a degree were inserted, one in the inner porous cell and another in the outer cell; and in cases in which a slight inequality of heating at the two electrodes occurred, a mean of the rise of temperature of the two thermometers was taken as best expressing the net heat-evolution.

The external battery, used for sending currents against the E.M.F. of the experimental cell, consisted of either a Daniell cell or a form of constant bichromate battery, in accordance with the E.M.F. of the experimental cell to be overcome. The current was measured by a calibrated galvanometer, which gave a deflexion of $47^{\circ}{\cdot}5$ with $\frac{1}{10}$ of an ampere, and was regulated by the introduction of the necessary resistance.

It was first proved in the case of a cell, cadmium-copper sulphate, which gives an E.M.F. almost exactly in accordance with its calculated value, that the heat which is generated by a current passing through the cell depends only upon its resistance, and is independent of the direction in which that current passes.

This being so, if the permanent experimental value of the E.M.F. of any cell differs by e volts from its calculated value ($E - E_h = \mp e$), an amount of heat equal to $\frac{ect}{J}$ ought to be evolved or absorbed when a current of strength c passes for t seconds through the cell.

Thus if the cell be one giving an excess, or $E - E_h = +e$, there should be an absorption of heat when the cell is worked forwards and an evolution when worked backwards against the E.M.F. of the cell. Exactly the reverse would hold with cells giving a deficit from the theoretical value.

Since the heat due to resistance will be evolved in both

cases, we have for the net heat evolved

$$H=\frac{c^2 r t \mp e c t}{J};$$

and where the value of $e c t$ is negative we have a negative total if it exceed the value of $c^2 r t$.

In order therefore that the *absorption* of heat may be a maximum, with cells giving an excess of E.M.F. when worked forwards, or with cells giving a deficiency when worked backwards, the current-strength must be adjusted in accordance with the determined value of the internal resistance of the particular cell.

Since the heat absorbed will be

$$-H_1=\frac{e c t-c^2 r t}{J},$$

or

$$-H_1 \propto e c-c^2 r,$$

and

$$\frac{dp}{dc}=e-2c r;$$

equating to maximum value we have

$$c=\frac{e}{2r}$$

as the current-strength giving the greatest absorption of heat in the case of a cell in which the computed and observed E.M.F.s differ by e volts and internal resistance is r ohms.

It is thus a matter of importance to determine the internal resistance, not only in order to be able to calculate the heat generated against it, but also to calculate the best current-strength for observing the effects. In many cells, however, the resistance is so unavoidably high that c would be too small for any thermal changes to be detected; and in other cases the current has to be increased above the best theoretical to a best practical strength, *time* being an important factor in such delicate thermal measurement.

It was found experimentally that the resistance in many cells is subject to considerable and, in some cases, enormous variations when currents are passing through the cell, being partly dependent upon the direction of the current. This forms one of the most serious difficulties in the experimental work, for if the resistance change with change of direction of

the current, the difference of heating-effects might be due, at least in certain cases, to such change rather than to the value of $E-E_h$.

This difficulty was endeavoured to be met by using a high resistance galvanometer on a circuit of several thousand ohms as a measurer of the difference of potential between the poles of the experimental cell, when on open circuit and when direct or inverse currents are passing through it.

Taking E as the E.M.F. of the external battery and R its resistance, and E_l the E.M.F. of the experimental cell, and r_l its resistance, and letting r_{ll} denote the total external resistance, including that of the current-galvanometer, we get for the difference of potentials between the poles of the experimental cell :

$$V=\frac{E_l(R+r_{ll})-E\,r_l}{R+r_l+r_{ll}} \text{ with direct currents,}$$

and

$$V_l=\frac{E_l(R+r_{ll})+E\,r_l}{R+r_l+r_{ll}} \text{ with inverse currents.}$$

Since, however, the value of E_l (or indeed E) is subject to possible variation due to polarization, the above method fails to distinguish between change of difference of potential due to change of resistance and that due to polarization ; and although the latter, if present, may be usually detected by suddenly interrupting the current and noting the value of E_l, the difficulty still remains to some extent and is liable to vitiate the results.

From the causes just indicated it will be readily seen that extremely few cells are suited for thermal experiments when currents of moderate strength have to be sent through them in alternate directions. Consequently a large number of voltaic combinations were tried and abandoned as unsatisfactory, for some of the following reasons :—Certain cells are found to give marked variation in their internal resistance with different direction of current, commonly owing to the sparing solubility of at least one of the salts formed and the consequent coating of one or both plates with insoluble and badly conducting films (*ex. gr.* cells involving the sulphate, chloride, or bromide of lead, mercury, or silver, three typi-

cally exceptional metals). In other cases cells are rendered useless by the imperfect reversibility of the chemical change; as in cases in which it is attempted to deposit a metal which can replace hydrogen from water at all readily (*ex. gr.* magnesium, aluminium, zinc, and iron), hydrogen is liable, in some cases certain, to be liberated in place of the equivalent of metal. In other cells, such as lead or silver in contact with their sulphates or free sulphuric acid, on making either of those metals the anode in the cell, a peroxide (PbO_2 or AgO) is apt to form in spots on the surface of the metal plate and entirely alter both the E.M.F. and resistance of the cell, besides obviously altering the chemical work of electrolysis.

The desiderata in a cell intended for this work—namely tolerable freedom from polarization, perfect reversibility, low and constant internal resistance—are only even approximately fulfilled by a very few of a large number of cells examined by me, and therefore the experimental results are greatly restricted.

Mercury.

After dismissing aluminium and magnesium as being unsuitable, for reasons already stated, the metal which has the next highest "thermovoltaic constant" positive in sign is mercury, and being the metal which is replaced by most other metals, as copper, zinc, &c., it yields electromotive forces considerably in excess of the values deduced from the heat of formation of its salts. The insolubility and sparing solubility of the mercurous chloride, bromide, and sulphate, and the inadmissibility of mercuric salts, owing to their reduction in contact with metallic mercury, rendered it necessary to employ mercurous nitrate, and, accordingly, a copper-mercury nitrate cell was prepared, in which each metal was in a strong solution of its own nitrate, with a small proportion of free nitric acid, which is necessary to keep the mercurous salt in solution by preventing the formation of basic salts, and also diminishes the internal resistance. I found this cell gave an E.M.F. of ·43 volt, while from the thermochemical numbers of Julius Thomsen, viz.

$[Cu, O, N_2O_5 Aq] = 52410$ and $[Hg_2, O, N_2O_5 Aq] = 47990$,

one would deduce an electromotive force of only ·095 volt.

(Wright and Thompson, adopting the older standards of measurement, give ·433 volt for the experimental and ·097 volt for the calculated value.)

When a current of ·2 ampere was passed in alternate directions through the cell, it was found that if the current was not continued for too long a period in one direction the resistance was moderately constant, though by the prolonged action of the current the solution became either nearly deprived of mercury, or saturated with mercurous nitrate in the layers near the metallic mercury, depositing crystalline nitrate on it and greatly increasing the resistance. But by allowing the current to pass for not more than 10 to 20 minutes in one direction this was avoided, and the rise of temperature which was observed corresponded very nearly with the heat due to $c^2 r t$, and was independent of the direction in which the current passed; showing therefore no absorption of heat with direct currents, as might be anticipated from its large excess of E.M.F., viz. ·335 volt.

This result was so plainly at variance with what was to be expected, that a solution of mercurous nitrate was electrolysed, using a platinum anode; but in this case also there was no indication of more chemical work being performed by the current than supplied by it, *i. e.* no absorption of heat was detected, but an evolution corresponding closely with the amount calculated from the values of $\frac{c^2 r t}{J}$. Hence the result of these experiments clearly pointed to the conclusion that mercury, if it be anomalous in its E.M.F., is not so on account of any transformation of sensible heat into electric energy; and I was therefore led to examine the thermochemical data of mercury upon which the calculated E.M.F.s have been founded.

Thermochemical Data of Mercury.

In the first place Julius Thomsen* appears to be the only experimentalist who has made determinations of the heats of formation of mercury salts, and since he depends upon the heat of formation of mercurous nitrate for the thermal values of almost all the other salts, if that were in error

* *Thermochemische Untersuch.* Band iii. S. 355.

all the values derived from it would evidently be equally inaccurate. But the method he employed for the determination of the heat of $[Hg_2, O, N_2O_5 Aq]$ does not appear to me entirely free from objection. He determined it by reducing the mercury from a solution of its nitrate by sulphur dioxide, and determined the heat of neutralization of $[Hg_2O, 2HNO_3 Aq]$ by decomposing the nitrate with sodic hydrate; finding, as above stated, 47990 calories for the heat of formation of the nitrate in aqueous solution. Since, however, mercurous nitrate requires the presence of free nitric acid to maintain it in solution, he used a solution containing free nitric acid to an extent variously stated as 1·079 and 3·079 HNO_3 per molecule of $Hg_2(NO_3)_2$; as the latter number is mentioned twice, probably the former is a misprint. But the exact reaction which occurs between mercurous nitrate, free nitric acid, and SO_2 one may reasonably expect to be less simple than that required for exact thermal measurement.

I have accordingly determined the heat of formation of mercurous nitrate in acid solution, by decomposing it with zinc amalgam, yielding zinc nitrate and metallic mercury; the results obtained are subjoined.

Mercury used.	Heat-units cooled.	Heat of Reaction.
1·362 grms.	265·5 grms ° C.	77,975
1·362 „	206·2 „	78,180
2·58 „	492·1 „	76,300
		Mean = 77,485

Since Thomsen finds 102 510 for $[Zn, O, N_2O_5 Aq]$, the heat of formation of

$$[Hg_2, O, N_2O_5 Aq] = 102{,}510 - 77{,}485 = 25{,}025 \text{ calories.}$$

If this be approximately true, it follows that the values given by Thomsen for the heats of formation of the chloride, bromide, and iodide of mercury must be greatly in excess of the true value. The heat of formation of $[Hg_2, Cl_2]$ is given by him as 82,550, taking 47,990 as the value for the nitrate. But it is well known that calomel is reduced to metallic mercury by an acid solution of stannous chloride, although the heat evolved in the conversion of $SnCl_2Aq$ into $SnCl_4Aq$ is only 76,030. Hence splitting up Hg_2Cl_2 with the forma-

tion of stannic from stannous chloride would give, according to Thomsen, the following thermal equation :—

$$[Sn\,Cl_2, Cl_2, Aq] - [Hg_2, Cl_2]$$
$$76{,}030 \quad - \quad 82{,}550 \quad = -6520,$$

so that this reaction would be markedly endothermic and could not well occur at ordinary temperatures.

The matter, however, was put to experimental test, and it was found that although the reaction was slow, requiring about three hours for its completion at a temperature of about 15° C., still heat was continuously *evolved*, and, after calculating for loss of heat, gave the following values :—

Weight of Hg_2Cl_2.	Heat evolved.	Heat of Reaction.
5·067 grms.	120·76 grms.° C.	11,225
4·783 „	104·8 „	10,325
		Mean = 10,775

Giving 76,030 − 10,775 = 65,255 calories as the heat of formation of Hg_2Cl_2.

The electromotive forces calculated from these thermal data give for zinc-mercury nitrate cells $E_h = 1{\cdot}673$ volt, the experimental value being 1·5 volt; and for zinc-mercury chloride cells $E_h = 1{\cdot}028$, the experimental value being 1·043 (Helmholtz), or from 1·123 to ·988 (Wright and Thompson). Hence it is evident that mercury cells do not evolve electromotive forces of about half a volt in excess of their calculated values, the various statements to that effect being based on inaccurate thermochemical data. On the contrary, it will be noticed that the value of E_h for the nitrate cell is greater than the experimental value E, which may be due to an error in my determination of the heat of formation of mercurous nitrate, but more probably to the same cause acting as in the cases of lead and silver, both of which metals have negative "thermovoltaic constants," and which greatly resemble mercury in many chemical characteristics.

Silver.

The "thermovoltaic constants" for silver, given by Wright and Thompson, vary from ·395, in the case of the nitrate, to ·02, in the case of the iodide, but are all negative in sign. It is noticeable that the larger values are attached to the

soluble salts, while the insoluble chloride, bromide, and iodide have much smaller "constants," and these depend largely on the nature of the liquid in which the haloid salt is suspended; thus AgCl in solution of $ZnCl_2$ has a thermovoltaic constant of ·112 to ·062 volt, while a copper-silver chloride cell in which the AgCl is suspended in $CuCl_2$ solution has a difference of only ·001 volt from the computed value. The causes producing the large divergence in the case of the nitrate or sulphate are, therefore, probably different in nature from those producing the small and very variable "constants" (?) in the case of the chloride, bromide, or iodide.

In order to test whether a cell consisting of silver in a solution of its nitrate, opposed to some other metal, gives rise to reversible heat-effects or not, a copper-silver nitrate cell was prepared and used in the manner previously described. It was found that when small currents (·1 to ·2 amp.) were sent in alternate directions through the cell by means of another battery, apart from the heat due to the square of the current and the resistance, there was an evolution of heat when the cell was worked forwards, and an absorption of heat when worked backwards so as to dissolve silver and deposit copper.

The following numbers, taken from one set of experiments, show the difference of heating with synergetic and opposed currents (E.M.F. of the cell ·431 to ·428 volt):—

	Mean rise of Temp.
Direct current of ·2 ampere for 20 minutes . .	0·6° C.
Adverse current " " . .	0·1° C.
Direct current " " . .	0·35° C.
Adverse current " " . .	0·00° C.
Direct current " " . .	0·45° C.
Adverse current " " . .	0·00° C.

Mean rise with direct currents $=0°{\cdot}466$ C.
Mean rise with adverse currents $=0°{\cdot}03$.
(Commonly $=0$).

The thermal capacity of the cell was determined and found to be equal to 68 grms. of water; so that

$$68 \times {\cdot}466 = 31{\cdot}688 \text{ grms.}^\circ \text{ C.}$$

represents the total mean heat evolved when the cell was worked forwards, and due to

$$\frac{c^2 r t + e c}{J}.$$

The mean resistance of the cell was found to be 1·4 ohm, and taking e, the difference between E and E_λ, as ·34 volt, we get

$$\frac{c^2 r t}{J} = \cdot 04 \times 1 \cdot 4 \times 1200'' \times \cdot 24 = 16 \cdot 1 \text{ grms.}^\circ \text{ C.}$$

and

$$\frac{e c t}{J} = \cdot 34 \times \cdot 2 \times 1200'' \times \cdot 24 = 19 \cdot 58 \text{ grms.}^\circ \text{ C.}$$

Hence the sum of these amounts, 35·68 grms.° C., and their difference, −3·48 grms.° C., represent the total amounts of heat evolved with direct and with adverse currents respectively, with which the experimental results of 31·69, and practically 0, accord within the limits of experimental error.

Hence it results that a copper-silver nitrate cell gives an electromotive force below the calculated value, and when it sends a current a portion of the energy due to the replacement of silver by copper appears as heat in the cell, and its equivalent in E.M.F. is therefore wanting. Consequently, when the cell is worked backwards, a smaller amount of work than that represented by the negative heat of substituting silver for copper is capable of producing the required electrolysis, the difference being supplied at the expense of sensible heat.

In view of the great difference in the heat of formation of mercury salts found by me, and the previously recorded values, I determined the heat of replacement of silver by copper from a solution of $AgNO_3$, $200H_2O$. The amount of silver was accurately determined both by titration of the solution and by calculation from the weight of the dissolved copper.

The results of two exactly similar experiments gave

I. = 33,420 calories,
II. = 33,450 calories,

as the heat of replacement :—

$$Cu + Ag_2(NO_3)_2 Aq = Cu(NO_3)_2 Aq + Ag_2.$$

These numbers are slightly below those found by Thomsen, he giving 35,630 as a mean; but they are sufficiently in agreement to show that the actual E.M.F. furnished by a copper-silver nitrate cell is considerably less than the calculated value.

It has been above remarked that the "thermovoltaic constants" of silver vary greatly with the salt of the metal employed, the soluble salts having much larger constants than the insoluble, and the latter diminishing to an insignificant quantity in the case of the iodide, or of the chloride suspended in cupric chloride. This would therefore show that it probably does not depend in any way upon the metal itself acting as a thermoelectric junction, but upon the nature of the chemical changes occurring in the cell.

From these, and other considerations which are given later, I conclude that the thermovoltaic constant depends upon two prime causes. One, which operates with both soluble and insoluble salts of silver, is a tendency of that metal to form subsalts, *e. g.* subchloride Ag_2Cl, the heat of formation of the equivalent of which is greater than that of the normal salt, so that silver is more readily attacked superficially and acquires a lower relative potential than would be predicted from the heat of formation of its normal salt.

Wetzlar has shown that silver-leaf immersed in solutions of cupric or ferric chloride becomes converted into Ag_2Cl, so that when a silver plate is immersed in cupric-chloride solution its surface rapidly becomes covered with a film of the subchloride of sufficient thickness to prevent the metallic silver producing its usual effect, and thus the thermovoltaic constant practically vanishes.

The other cause of divergence is of much wider application, and appears to me to depend upon the fact that with any salt, such as silver nitrate, which does not form a hydrate with water, but being soluble absorbs heat on dissolving, this heat can be supplied by the thermometric heat of surrounding bodies, and one would expect it to be "bound energy," and to be a reversible thermal effect independent of the effects due to the "free energy" of the chemical change.

Since the heat of solution of silver nitrate is a large negative quantity, -5440 or $-10{,}880$ for $Ag_2(NO_3)_2$,Aq, the heat

of formation of anhydrous $AgNO_3$ would be greater by that amount than that measured when using its solutions. This would give the heat of formation of

$$[Ag_2, O, N_2O_5] = 16,770 + 10,880 = 27,650,$$

and thus give a calculated E.M.F. about ·235 volt lower, still leaving a deficiency of about ·105 volt to be accounted for by the tendency of silver to form a film of subsalt; unless indeed the heat of formation of silver nitrate has been under-estimated, as the numbers given above for the heat of replacement of silver by copper might indicate.

These numbers, after allowance for the negative heat of solution of silver nitrate, would give a calculated electromotive force almost exactly in agreement with the experimental value.

Lead.

Lead, like silver, is a metal having a large negative "thermovoltaic constant," which also varies with the salt of the metal employed. Wright and Thompson give for the difference of E and E in the case of lead in saturated solutions of its chloride and bromide ·222 and ·235 volt, while for the iodide only ·002 volt. This difference, however, is readily explained on reference to the numbers selected by these authors in calculating the theoretical E.M.F., as, in the case of the chloride and bromide, they employ the heats of formation of the dissolved salts, while they use the heat of formation of solid lead iodide. Inasmuch as they used *saturated* solutions of the chloride and bromide, it is difficult to see why they selected the values corresponding to the dissolved salts, since any more salt formed must necessarily be produced in the solid state, and the electromotive force would, consequently, be determined by the heat of formation of the solid salts.

Further, since there is no chemical attraction between these compounds and water, and there is merely an absorption of heat on solution, in accordance with the view stated above (in regard to silver nitrate), the E.M.F. will depend upon the heat of formation of the solid salt, even though the solution be not saturated.

The values calculated from the dissolved and anhydrous salts and the experimental values are compared below :—

		Observed Average Value.
$[Zn, Cl_2, Aq]-[Pb, Cl_2, Aq]$	$=36870$ c. $=\cdot796$ volt	Volt.
$[Zn, Cl_2, Aq]-[Pb, Cl_2]$	$=30070$ c. $=\cdot649$ volt	$\cdot591$
$[Zn, Br_2, Aq]-[Pb, Br_2, Aq]$	$=36550$ c. $=\cdot789$ volt	$\cdot571$
$[Zn, Br_2, Aq]-[Pb, Br_2]$	$=26510$ c. $=\cdot572$ volt	

The zinc-lead iodide cell being calculated from the heat of formation of solid PbI_2 accords almost exactly with the experimental value, the difference being only ·002 volt.

Similarly with a zinc-lead nitrate cell, while the E.M.F. calculated from the heat of dissolved lead nitrate is ·737 volt, after allowing for the large negative heat of solution, −7600, one gets for $[Zn,O,N_2O_5,Aq]-[Pb,O,N_2O_5]$, 102,510−(68,070 +7600)=26,840, giving a calculated E.M.F. of ·580 volt, which agrees exactly with the experimental value ·580 to ·591 volt.

A reference to the effect of concentration of the solutions on the electromotive force of a zinc-lead nitrate cell confirms my views. Wright and Thompson find that increasing the solution strength from ·25 to $2M''(NO_3)_2$, $100H_2O$ causes an increase in the E.M.F. from ·580 to ·591, while they calculate that it should decrease from ·759 to ·716. Hence, instead of a *fall* of ·043 volt there is a *rise* of ·011 volt, the cause of the increase being in all probability due to the fact that the heat of dilution of zinc nitrate is positive in strong but negative in weak solutions; so that with moderately strong solutions the whole of the combining energy of zinc nitrate with water may be converted into electric energy, while in weak solutions a portion of that part of the energy of chemical change is expended in the absorption of heat due to the greater dilution of the salt.

It may be well to give here some collateral evidence in support of this view. In the first place, if lead in chloride solutions, either not saturated with or entirely free from *lead* chloride, had a tendency to form $PbCl_2$, represented by the heat of formation of the dissolved salt, viz. 75,970 c., this metal should be without action on a solution of stannous chloride, the heat of formation of which in aqueous solution is 81,140 calories; but, as a matter of fact, a piece of pure clean lead placed in an acid solution of stannous chloride

becomes immediately covered with a dull grey film, and after a short time small brilliant crystals of deposited tin appear all over its surface. For the same reason a cell consisting of lead and tin plates, both immersed in either dilute hydrochloric acid, stannous chloride, or lead chloride solutions, furnishes a current the direction of which indicates that lead and not tin is the metal attacked, the actual E.M.F. being about ·008 to ·012 volt. On the other hand, pure tin will not remove lead from solutions of its nitrate or acetate or cold solutions of its chloride, though if an acid solution of lead chloride be boiled with tin, lead is deposited to a slight extent. Similarly the above lead-tin cell, using an acid solution of stannous chloride, will be found to diminish in E.M.F. as its temperature is raised, so that between 50° and 60° C. it possesses no E.M.F., while above that temperature the current flows in the reversed direction, tin being the metal attacked. This explains why an alloy of lead and tin, when treated with hot hydrochloric acid, yields a solution of stannous chloride, leaving the lead unattacked. That the non-production of lead chloride cannot be due to the prospective absorption of heat on dissolving *after its formation* appears sufficiently evident; and I think this reversed action at the higher temperature is to be explained by the heat of formation of the compound $SnCl_2 2H_2O$ being greater than that of even solid lead chloride (viz. 86,510 and 82,550 respectively); and although the former would be dissolved with a certain absorption of heat dependent on the strength of solution and the temperature, this amount would be less than the 5370 calories absorbed at low temperatures and in dilute solutions, and, further, being due to the merely physical process of solution, may at the high temperature be supplied largely at the expense of sensible heat, instead of being deducted from the energy of the chemical change.

Nickel is a metal in the formation of the anhydrous chloride of which 74,530 calories are evolved, while in aqueous solution it furnishes 93,700 calories. If, therefore, the heat of formation of the dry salt plus the heat of hydration be regarded as measuring the total chemical energy and as occurring together, nickel should be able to replace tin or lead from their chloride solutions. But, as a matter of fact, instead of this being the case, pure electro-deposited tin is

capable of completely displacing nickel from a solution of its chloride containing free hydrochloric acid, when allowed to remain in contact for a considerable time ; and on boiling the mixture of tin and deposited nickel in hydrochloric acid, tin and not nickel is dissolved. Nitric acid, however, rapidly attacks the nickel.

This result is at once explained on reference to the heat of formation of anhydrous nickel chloride, which, as above stated, is given by Thomsen as 74,530, while the heat of formation of stannous chloride is 81,140 in aqueous solution, or 80,790 if anhydrous. The heat which would on the whole be absorbed by this replacement in aqueous solution would doubtless be supplied by surrounding temperature.

These considerations, therefore, show that the heat of formation of the anhydrous salt is the most important factor in determining the chemical reaction, and suggest that the kind of energy set free in the formation of a dry salt differs from that due to the hydration of that salt, the latter being only partly "free energy," while the negative heat of simple solution may be supplied entirely by the "bound energy" of the chemical change.

A similar explanation will account for the fact that an iron-cadmium chloride cell gives an E.M.F. opposite in direction to that anticipated from the heats of formation of their salts in solution, since Thomsen gives $[Cd,Cl_2] = 93{,}240$, $[Cd, Cl_2, Aq] = 96{,}250$, and $[Fe, Cl_2] = 82{,}050$, $[Fe, Cl_2, Aq] = 99{,}950$.

Thus, taking the anhydrous salts we get a difference of 11,190 on the side of cadmium, while taking the dissolved salts gives 3700 calories in favour of iron being attacked and depositing cadmium, which is known not to occur. Thus the first action in point of time—the formation of the anhydrous salt—directs the course of the chemical change, which, however, in the present case is not a replacement of iron by cadmium, but if a current flow, hydrogen is evolved on the iron plate ; so that this cell does not reverse the expected reaction and furnish a current at the expense of sensible heat, but, owing to the initial difference in the heats of formation of the dry salts, an entirely different reaction is started and continued.

It is owing to the fact that iron is not deposited electrolytically from neutral or acid solutions of its salts that its large positive constant was referred earlier in this paper to a false reaction, though the above consideration shows at least one cause for its anomalous behaviour.

Tin.

Measurements of the electromotive force of cells in which tin in a solution of its chloride is opposed to other metals having shown * that it possesses an apparent negative "thermovoltaic constant," it was resolved to employ a cell in which tin is the metal attacked, and which should consequently give an E.M.F. in excess of the heat evolution due to the chemical change. Copper, which naturally suggests itself as the opposing metal, is, however, very unsatisfactory for thermal measurements when used in a solution of its chloride, owing to the production of cuprous chloride on its surface, and further, as Thomsen found for the heat of replacement of tin by zinc from solution of its chloride numbers varying from 28,940 to 33,510 calories (a variation of 4570 calories, or ·098 volt), a determination of the previously unknown heat of formation of stannous sulphate was made with the object of using a tin-copper sulphate cell.

A solution of copper sulphate, each cubic centimetre of which contained ·015875 grm. of copper, corresponding to ·45Cu SO_4 $100H_2O$, and containing free sulphuric acid to the extent of 2 per cent., was treated in the calorimeter with excess of pure granulated tin ; the copper was speedily deposited, and the following heat measurements were made :—

Weight of Copper.	Heat evolved.	Heat of Reaction.
·635 grm.	190·36 grm.° C.	19,036 calories.
·635 „	193·14 „	19,314 „
·635 „	193·98 „	19,398 „
	Mean . .	19,250 „

As Thomsen finds for the heat of formation of copper sulphate 55,960, this number added to 19,250 gives the heat of formation of [Sn, O, SO_3 Aq] = 75,210 c.

* Phil. Mag. ser. 5, vol. xxi p. 13.

In the above reaction there was no evolution of hydrogen gas, even after the whole of the copper had been deposited, and the conditions were as similar as possible to those obtaining in the case of the same replacement in the voltaic cell. But in the next experiment, which was conducted partly as a control on the previous values, a small amount of hydrogen was produced towards the end of the reaction. The solution of stannous sulphate obtained in the previous reaction was decomposed by placing in it strips of pure cadmium, and the heat of the reaction $Sn\,SO_4Aq + Cd = CdSO_4Aq + Sn$ was accordingly measured, giving 15,210 c. as the result. Since $[Cd, O, SO_3\,Aq] = 89{,}880$, the difference $89{,}880 - 15{,}210 = 74{,}670$ represents the heat of formation of $[Sn, O, SO_3\,Aq]$, as measured in this way, and agrees fairly well with the result obtained by the replacement of copper by tin, but is slightly lower, probably owing to the above-mentioned slight evolution of hydrogen, and therefore excess of the heat of replacement of tin by cadmium.

As a further check upon the general method I determined the heat of replacement of copper by zinc, using the same solution, viz. $\cdot 45CuSO_4\ 100H_2O$, but, of course, free from sulphuric acid, and found the heat of reaction to be 50,980 c., the number calculated from Julius Thomsen's values being 50,130 for solutions containing $\cdot 25CuSO_4 100H_2O$, which numbers I considered to be in sufficiently close agreement.

But adopting 19,250 c. as the heat of replacement of copper by tin we get a calculated E.M.F. of only ·416 volt, while experiment shows an E.M.F. of ·55 volt as a mean value; thus showing that a tin-copper sulphate cell furnishes an E.M.F. of about ·144 volt in excess of its computed value. Using this cell in a calorimeter, I found that with direct currents of ·1125 ampere passing through the cell there was an absorption of heat, and when worked backwards against the E.M.F. of the cell there was an evolution of heat apart from that due to the square of the current and the resistance. The internal resistance in one of these cells was reduced to only ·9 ohm, so that the heat due to it was very small.

I conclude from these observations, and in consonance with the theory already stated, that stannous sulphate has a negative heat of dilution, which portion of its total energy, while

appearing as negative in the calorimeter, is unable to reduce the electromotive force due to the "free energy" of the undiluted salt, the negative heat of dilution being supplied by fall of temperature. I have not been able to verify this conclusion experimentally, and the subject is complicated by the necessity of having free acid present in its solutions to prevent the formation of basic salts. The effect both of dilution and of the quantity of free acid present also greatly influence the E.M.F. of stannous chloride cells, and some points in regard to its action may be seen from the following consideration.

It is well known that if a strip of tin be placed vertically in a vessel, containing at its lower part a strong solution of stannous chloride (with free hydrochloric acid) and above it water, at the line of junction of the liquids, where a dilute solution of stannous chloride is formed by the intermixture, metallic tin is deposited in brilliant crystals on the tin plate, tin dissolving in the liquid below. This solution of a metal in a concentrated solution of one of its salts and its deposition from a dilute one is entirely contrary to what would be expected, were it not for the fact that in the relatively strong hydrochloric acid in the lower liquid there is a store of potential chemical energy which may either evolve heat in diffusion and dilution, or, by attacking the tin plate in contact with it, furnish a current which, flowing through the liquid and metal, has the effect of depositing an equivalent amount of tin from the solution above, in which the hydrochloric acid, being more dilute, has less tendency to dissolve the tin, a considerable portion of its energy having already been expended in the heat evolved during dilution.

Hence in tin cells, while I recognize a negative "thermo-voltaic constant" which is capable of producing reversible thermal effects in the cell, I am inclined to refer them to two causes: (α) a negative heat of dilution of the salts, and (β) to effects of differences of concentration of the acid necessarily employed to keep the salt in solution*.

* In my previously published measurements of the E.M.F. of tin cells the value given for the cadmium-tin sulphate cell was only ·189 volt; but I have since found that, using more dilute and less acid solutions, a persistent value as high as ·234 volt may be obtained.

General Conclusions.

A review of the published measurements of the thermal values of chemical reactions, in particular those directly relating to electromotive forces, namely, the replacement of one metal by another from its dissolved salt, will, I think, show that however valuable they may be as guides they cannot be implicitly relied upon as furnishing absolute and unimpeachable data by which to judge the truth or fallacy of a given theoretical conclusion. In the first place, in the numbers representing the heat of formation of the same body, determined by different experimenters, there are frequently discrepancies of considerable magnitude. Thus Thomsen finds for the heat of reaction of lead acetate and zinc 34,950 cal., Favre finding only 31,200 c., while Andrews gave 37,710 c.; a total variation between the extremes of 6,510 calories. For the heat of formation of CuO, and therefore of all salts derived from it, Thomsen gives 37,160, Favre and Silbermann 43,770, and Andrews 38,300, while [Fe, Cl_2, Aq] is variously estimated by Thomsen at 99,950, by Favre and Silbermann at 106,700, and by Andrews at 102,060.

Besides these experimental differences there is always the fact that, as Berthelot has clearly laid down in his introduction to his *Essai de mécanique chimique*, the quantity of heat evolved in a reaction measures *the sum of the physical and chemical changes* which occur in the reaction ; some of which quantities may be positive or negative, and which may or may not directly influence the transformable energy of the chemical change.

Adopting the view of Helmholtz that a chemical process gives rise to a total amount of energy, part of which is freely transformable and part of which is "bound energy," while the calorimeter measures the total energy, the electromotive force of a voltaic cell is a measure of the actual transformation of free energy. In cases, therefore, in which a portion of the total energy is to be reckoned as negative in respect to the main reaction, we see that such portion may be supplied either at the expense of the free or of the bound energy. If performed by the free energy, obviously the amount of that energy which could appear in

other forms must be proportionately reduced ; while if performed at the expense of the bound energy, merely thermal effects would follow, without affecting the course or amount of the free-energy stream. It follows that in certain cases, as for instance in the case of lead nitrate, or silver nitrate, if the heat of solution is a large negative quantity, the free energy, in my opinion, is greater than the total energy, since the bound energy is negative in sign ; but, assuming that this negative bound energy is not supplied at the expense of the free energy, it can be readily made up by thermometric heat. Hence, while thermal measurements indicate $27{,}600 - 10{,}880 = 16{,}720$ as the heat of formation of silver nitrate in solution, the voltaic cell shows that at least 27,600 thermal units must be regarded as transformable free energy, the 10,880 negative heat-units being abstracted not from it, but from sensible heat. On the whole there must be an increase of entropy, but there may be an absorption of heat, as when a lead-copper nitrate cell sends a current, or a copper-silver cell is worked backwards.

The partial independence of thermal effects due to concentration of solutions and electromotive forces, is recognized by Helmholtz when he states in the case of a Latimer Clark cell with saturated zinc-sulphate solution, that "the zinc sulphate, newly formed by the current, can no longer be dissolved, and its latent heat of solution is saved ; accordingly there is *a more powerful development of heat in the cell in spite of the weaker electromotive force.*" His theoretical mathematical treatment disposes of many difficulties, but it did not prevent him from the error of believing that mercury, when deposited by zinc, even from its solid salts, gave rise to an E.M.F. largely in excess of the thermal values, which, according to my view, would be quite impossible, as it would amount to a conversion not merely of "bound energy" into "free energy," but, under special circumstances of the thermometric heat, into higher forms of energy with the production of mechanical effect.

It might be thought that the whole of the heat liberated in the formation of the fully hydrated salt was a measure of the available energy, and that the negative heats of dilution were supplied solely at the expense of sensible heat, but this

supposition is entirely negatived by the actual electromotive forces of several cells (*ex. gr.* zinc-cadmium bromide cell); so that I conclude that since the hydration and solution of a newly formed salt will, to a great extent, occur simultaneously, the heat of hydration is partly absorbed in the process of solution and dilution, and therefore to that extent cannot furnish electrical energy. On the other hand, when a salt is used which does not form hydrates, and consequently can *only* absorb heat during solution, the energy due to the formation of the solid salt determines the E.M.F., which cannot be subsequently decreased by a process which has no chemical continuity with it, but which merely absorbs sensible heat.

As Helmholtz has already remarked, the exact reversibility of these processes indicates the constancy of the partition of "free" and "bound," or electrogenic and thermogenic energy, and negatives the earlier supposition of Braun that the proportion of transformable energy was the accident of circumstances.

Helmholtz has further shown that, regarding the energy and entropy of a system undergoing a restricted change as represented by the differential coefficients of an integral function of the system or substance, under the usual conditions the performance of external work takes place at the expense of the "*free energy*," while loss of heat at the expense of the "*bound energy*." But whether there subsists a definite relation between the freely transformable and the bound energy on the one hand, and on the other hand between that portion of the energy set free by the process of hydration of a salt which is convertible into electric energy, and that portion which runs down into heat, is a question which appears to demand careful experimental as well as mathematical consideration ; especially with reference to the influence of temperature and various degrees of concentration of the salt.

The fact that the E.M.F. of a cell, like zinc-cadmium chloride, does not increase with greater dilution as rapidly as it should from thermochemical considerations, may be taken as indicating that the degradation of energy of the system increases as the number of water-molecules in which the salt is dissolved is augmented.

I conclude, therefore, that :—

I. The primary factor in determining the electromotive force of a voltaic cell is the relative heat of formation of the anhydrous salts of the two metals employed.

II. That the E.M.F. may set up chemical changes of a different direction and character from those predicable from the heat of formation of the dissolved salts.

III. That the E.M.F. set up by (I.) may be, and usually is, supplemented by the energy, or a portion of the energy, due to the hydration or solution of the solid salts, and may have values which accord with the heat of formation of the dissolved salts.

IV. That in those cases in which there is no chemical attraction, or a very feeble attraction between the water and the salt, the negative heat of solution is derived from sensible heat, and is not supplied by the free energy of the chemical change. All cells in which such salts are employed opposed to zinc should have *negative* "thermovoltaic constants," and evolve heat when they send a current forwards.

V. That when metals, whose salts have purely negative heats of solution, are opposed to metals whose salts they can replace, the E.M.F. set up is *in excess* of the total thermal change. Such cells, therefore, absorb sensible heat when worked forwards.

VI. That, taking the foregoing facts into consideration, no cell exists which can furnish an E.M.F. in excess of the free energy of the chemical change; *i.e.* which can convert sensible heat into electric energy working at uniform temperature. (Negatives the supposition concerning mercury and other cells.)

VII. That certain metals have a tendency to form films of sub-salts on their surfaces, the formation of which giving rise, as it does, to a different thermochemical reaction, naturally furnishes an E.M.F. which does not correspond with the values calculated from the heats of formation of their normal salts. (*Ex. gr.* copper in cupric chloride, mercury in mercuric chloride, probably silver in most soluble chlorides.)

VIII. That the electromotive force of a voltaic cell furnishes a more accurate measurement of the "free energy," and therefore of true chemical affinity, than data derived from calorimetric observations.